
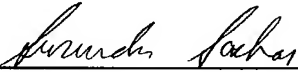


FORM PTO-1390 (Modified) (REV 11-2000)		U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE		ATTORNEY'S DOCKET NUMBER <b>220975US0PCT</b>	
<b>TRANSMITTAL LETTER TO THE UNITED STATES</b> <b>DESIGNATED/ELECTED OFFICE (DO/EO/US)</b> <b>CONCERNING A FILING UNDER 35 U.S.C. 371</b>				U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR <div style="font-size: 1.5em; font-family: monospace;">10/088904</div>	
INTERNATIONAL APPLICATION NO. <b>PCT/JP00/06645</b>		INTERNATIONAL FILING DATE <b>27 September 2000</b>		PRIORITY DATE CLAIMED <b>27 September 1999</b>	
TITLE OF INVENTION <b>GRAFT COPOLYMER AND THERMOPLASTIC RESIN COMPOSITION CONTAINING THE GRAFT COPOLYMER</b>					
APPLICANT(S) FOR DO/EO/US <b>Yoshihiro NAKAI et al.</b>					
Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:					
<ol style="list-style-type: none"> <li>1. <input checked="" type="checkbox"/> This is a <b>FIRST</b> submission of items concerning a filing under 35 U.S.C. 371.</li> <li>2. <input type="checkbox"/> This is a <b>SECOND</b> or <b>SUBSEQUENT</b> submission of items concerning a filing under 35 U.S.C. 371.</li> <li>3. <input checked="" type="checkbox"/> This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (24) indicated below.</li> <li>4. <input checked="" type="checkbox"/> The US has been elected by the expiration of 19 months from the priority date (Article 31).</li> <li>5. <input checked="" type="checkbox"/> A copy of the International Application as filed (35 U.S.C. 371 (c) (2))           <ol style="list-style-type: none"> <li>a. <input type="checkbox"/> is attached hereto (required only if not communicated by the International Bureau).</li> <li>b. <input checked="" type="checkbox"/> has been communicated by the International Bureau.</li> <li>c. <input type="checkbox"/> is not required, as the application was filed in the United States Receiving Office (RO/US).</li> </ol> </li> <li>6. <input checked="" type="checkbox"/> An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).           <ol style="list-style-type: none"> <li>a. <input checked="" type="checkbox"/> is attached hereto.</li> <li>b. <input type="checkbox"/> has been previously submitted under 35 U.S.C. 154(d)(4).</li> </ol> </li> <li>7. <input checked="" type="checkbox"/> Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371 (c)(3))           <ol style="list-style-type: none"> <li>a. <input type="checkbox"/> are attached hereto (required only if not communicated by the International Bureau).</li> <li>b. <input type="checkbox"/> have been communicated by the International Bureau.</li> <li>c. <input type="checkbox"/> have not been made; however, the time limit for making such amendments has NOT expired.</li> <li>d. <input checked="" type="checkbox"/> have not been made and will not be made.</li> </ol> </li> <li>8. <input type="checkbox"/> An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).</li> <li>9. <input checked="" type="checkbox"/> An oath or declaration of the inventor(s) (35 U.S.C. 371 (c)(4)).</li> <li>10. <input type="checkbox"/> An English language translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371 (c)(5)).</li> <li>11. <input type="checkbox"/> A copy of the International Preliminary Examination Report (PCT/IPEA/409).</li> <li>12. <input checked="" type="checkbox"/> A copy of the International Search Report (PCT/ISA/210).</li> </ol>					
<b>Items 13 to 20 below concern document(s) or information included:</b>					
<ol style="list-style-type: none"> <li>13. <input checked="" type="checkbox"/> An Information Disclosure Statement under 37 CFR 1.97 and 1.98.</li> <li>14. <input type="checkbox"/> An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.</li> <li>15. <input checked="" type="checkbox"/> A <b>FIRST</b> preliminary amendment.</li> <li>16. <input type="checkbox"/> A <b>SECOND</b> or <b>SUBSEQUENT</b> preliminary amendment.</li> <li>17. <input type="checkbox"/> A substitute specification.</li> <li>18. <input type="checkbox"/> A change of power of attorney and/or address letter.</li> <li>19. <input type="checkbox"/> A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825.</li> <li>20. <input type="checkbox"/> A second copy of the published international application under 35 U.S.C. 154(d)(4).</li> <li>21. <input type="checkbox"/> A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).</li> <li>22. <input type="checkbox"/> Certificate of Mailing by Express Mail</li> <li>23. <input checked="" type="checkbox"/> Other items or information:</li> </ol>					
<b>Notice of Priority/ Form PTO-1449</b> <b>PCT/IB/304/ References Cited (4)</b> <b>Statement of Relevancy</b>					

25 MAR 2002

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR 101.101) <b>10/088904</b>		INTERNATIONAL APPLICATION NO. <b>PCT/JP00/06645</b>		ATTORNEY'S DOCKET NUMBER <b>220975US0PCT</b>	
24. The following fees are submitted:				CALCULATIONS PTO USE ONLY	
<b>BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)) :</b>					
<input type="checkbox"/> Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO . . . . .				\$1040.00	
<input checked="" type="checkbox"/> International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO . . . . .				\$890.00	
<input type="checkbox"/> International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO . . . . .				\$740.00	
<input type="checkbox"/> International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4) . . . . .				\$710.00	
<input type="checkbox"/> International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4) . . . . .				\$100.00	
<b>ENTER APPROPRIATE BASIC FEE AMOUNT =</b>				<b>\$890.00</b>	
Surcharge of \$130.00 for furnishing the oath or declaration later than <input type="checkbox"/> 20 <input checked="" type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492 (e)).				<b>\$130.00</b>	
CLAIMS		NUMBER FILED		NUMBER EXTRA	
Total claims		21 - 20 =		1	
Independent claims		2 - 3 =		0	
Multiple Dependent Claims (check if applicable).		<input type="checkbox"/>			
<b>TOTAL OF ABOVE CALCULATIONS =</b>				<b>\$1,038.00</b>	
<input type="checkbox"/> Applicant claims small entity status. See 37 CFR 1.27). The fees indicated above are reduced by 1/2.				<b>\$0.00</b>	
<b>SUBTOTAL =</b>				<b>\$1,038.00</b>	
Processing fee of \$130.00 for furnishing the English translation later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492 (f)).				<b>\$0.00</b>	
<b>TOTAL NATIONAL FEE =</b>				<b>\$1,038.00</b>	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31) (check if applicable).				<input type="checkbox"/>	
<b>TOTAL FEES ENCLOSED =</b>				<b>\$1,038.00</b>	
				Amount to be: refunded \$	
				charged \$	
a. <input checked="" type="checkbox"/> A check in the amount of <u>\$1,038.00</u> to cover the above fees is enclosed.					
b. <input type="checkbox"/> Please charge my Deposit Account No. _____ in the amount of _____ to cover the above fees. A duplicate copy of this sheet is enclosed.					
c. <input checked="" type="checkbox"/> The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. <u>15-0030</u> A duplicate copy of this sheet is enclosed.					
d. <input type="checkbox"/> Fees are to be charged to a credit card. <b>WARNING:</b> Information on this form may become public. <b>Credit card information should not be included on this form.</b> Provide credit card information and authorization on PTO-2038.					
<b>NOTE:</b> Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.					
SEND ALL CORRESPONDENCE TO:					
<div>Surinder Sachar Registration No. 34,423  <b>22850</b></div> <div> SIGNATURE <b>Norman F. Oblon</b> NAME <b>24,618</b> REGISTRATION NUMBER <u>March 25 2002</u> DATE</div>					

220975US-0PCT

#4/a

IN THE UNITED STATES PATENT & TRADEMARK OFFICE

IN RE APPLICATION OF: :  
YOSHIHIRO NAKAI ET AL. :  
SERIAL NO: NEW U.S. PCT APPLN. : ATTN: APPLICATION BRANCH  
(Based on PCT/JP00/06645)  
FILED: HEREWITH :  
FOR: GRAFT COPOLYMER AND THERMO-  
PLASTIC RESIN COMPOSITION  
CONTAINING THE GRAFT COPOLYMER

PRELIMINARY AMENDMENT

ASSISTANT COMMISSIONER FOR PATENTS  
WASHINGTON, D.C. 20231

SIR:

Prior to examination on the merits, please amend the above-identified application as follows.

IN THE CLAIMS

Please amend the claims as shown on the marked-up copy following this amendment to read as follows.

13. (Amended) A thermoplastic resin composition comprising 1-100% by weight of the graft copolymer (G) of claim 1, 99-0% by weight of the other graft copolymer (S) and/or the other thermoplastic resin (F) (total of 100% by weight).

14. (Amended) A thermoplastic resin composition according to claim 13, wherein said other thermoplastic resin (F) is at least one selected from the group consisting of acrylic resin, acrylonitrile-styrene (AS) resin, acrylonitrile-styrene-N-substituted maleimide

[illegible]REMARKS

Claims 1-21 are active in the present application. Claims 13 and 14 have been amended to correct a typographical or clerical error. Support for the amendment is found throughout the specification, for example on page 9, lines 7-8. No new matter is believed to have been added by this amendment. An action on the merits and allowance of claims is solicited.

Respectfully submitted,

OBLON, SPIVAK, McCLELLAND,  
MAIER & NEUSTADT, P.C.

Shoschmedon

Norman F. Oblon  
Attorney of Record  
Registration No. 24,618

Stefan U. Koschmieder, Ph.D.  
Registration No. 50,238



**22850**

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NFO/DJP/smi

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220975US-0PCT

<b>Marked-Up Copy</b>
Serial No: _____
Amendment Filed on: _____
3-25-2002

IN THE CLAIMS

Please amend the claims as follows.

--13. (Amended) A thermoplastic resin composition comprising 1-100% by weight of the graft copolymer (G) of claim 1, 99-0% by weight of the other graft copolymer (S) and/or the other thermoplastic resin [composition] (F) (total of 100% by weight).

14. (Amended) A thermoplastic resin composition according to claim 13, wherein said other thermoplastic resin [composition] (F) is at least one selected from the group consisting of acrylic resin, acrylonitrile-styrene (AS) resin, acrylonitrile-styrene-N-substituted maleimide terpolymer, styrene-maleic anhydride copolymer, styrene-maleic anhydride-N-substituted maleimide terpolymer, acrylonitrile-styrene-(meth)acrylate terpolymer, polyolefin resin, polyvinyl chloride resin, polystyrene resin, polyamide resin, polyester resin, polycarbonate resin, polyphenylene ether resin, polyacetal resin, polyarylate resin, polyphenylene sulfide resin, polyether ether ketone resin (PEEK resin), and polyether sulfone resin (PES resin).--

DOCKET NO.: 220975US0PCT

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

IN RE APPLICATION OF: Yoshihiro NAKAI, et al.

SERIAL NO.: NEW U.S. PCT APPLICATION

FILED: HEREWITH

INTERNATIONAL APPLICATION NO.: PCT/JP00/06645

INTERNATIONAL FILING DATE: September 27, 2000

FOR: GRAFT COPOLYMER AND THERMOPLASTIC RESIN COMPOSITION CONTAINING  
THE GRAFT COPOLYMER

**REQUEST FOR PRIORITY UNDER 35 U.S.C. 119**  
**AND THE INTERNATIONAL CONVENTION**

Assistant Commissioner for Patents  
Washington, D.C. 20231

Sir:

In the matter of the above-identified application for patent, notice is hereby given that the applicant claims as priority:

**COUNTRY**

Japan

**APPLICATION NO**

11-273462

**DAY/MONTH/YEAR**

27 September 1999

Certified copies of the corresponding Convention application(s) were submitted to the International Bureau in PCT Application No. PCT/JP00/06645. Receipt of the certified copy(s) by the International Bureau in a timely manner under PCT Rule 17.1(a) has been acknowledged as evidenced by the attached PCT/IB/304.

Respectfully submitted,  
OBLON, SPIVAK, McCLELLAND,  
MAIER & NEUSTADT, P.C.



Norman F. Oblon  
Attorney of Record  
Registration No. 24,618  
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JC13 Rec'd PCT/PTO 25 MAR 2002

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(OSMMN 10/01)

Docket No. 220975US0PCT

IN RE APPLICATION OF: Yoshihiro NAKAI, et al.

SERIAL NO: New U.S. PCT Application

FILED: HEREWITH

FOR: GRAFT COPOLYMER AND THERMOPLASTIC RESIN COMPOSITION CONTAINING THE GRAFT COPOLYMER

ASSISTANT COMMISSIONER FOR PATENTS  
WASHINGTON, D.C. 20231

SIR:

Transmitted herewith is an amendment in the above-identified application.

- ☒ No additional fee is required
- ☐ Small entity status of this application under 37 C.F.R. §1.9 and §1.27 is claimed.
- ☒ Additional documents filed herewith: PCT Transmittal Letter/ Notice of Priority/ PCT/IB/304/ References Cited (4)  
Information Disclosure Statement/Form PTO-1449/International Search Report

The Fee has been calculated as shown below:

CLAIMS	CLAIMS REMAINING		HIGHEST NUMBER PREVIOUSLY PAID	NO. EXTRA CLAIMS	RATE	CALCULATIONS
TOTAL	21	MINUS	21	0	× \$18 =	\$0.00
INDEPENDENT	2	MINUS	3	0	× \$84 =	\$0.00
		<input type="checkbox"/> MULTIPLE DEPENDENT CLAIMS			+ \$280 =	\$0.00
		TOTAL OF ABOVE CALCULATIONS				\$0.00
		<input type="checkbox"/> Reduction by 50% for filing by Small Entity				\$0.00
		<input type="checkbox"/> Recordation of Assignment			+ \$40 =	\$0.00
		TOTAL				\$0.00

☐ A check in the amount of **\$0.00** is attached.

☒ Please charge any additional Fees for the papers being filed herewith and for which no check is enclosed herewith, or credit any overpayment to deposit Account No. 15-0030. A duplicate copy of this sheet is enclosed.

☒ If these papers are not considered timely filed by the Patent and Trademark Office, then a petition is hereby made under 37 C.F.R. §1.136, and any additional fees required under 37 C.F.R. §1.136 for any necessary extension of time may be charged to Deposit Account No. 15-0030. A duplicate copy of this sheet is enclosed.

OBLON, SPIVAK, McCLELLAND,  
MAIER & NEUSTADT, P.C.

*Norman F. Oblon*  
Norman F. Oblon  
Registration No. 24,618

Surinder Sachar  
Registration No. 34,423



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(OSMMN 10/01)



## DESCRIPTION

### GRAFT COPOLYMER AND THERMOPLASTIC RESIN COMPOSITION CONTAINING THE GRAFT COPOLYMER

#### TECHNICAL FIELD

The present invention relates to a thermoplastic resin composition having excellent weather resistance, impact resistance, fluidity, and gloss of molding, in which gas evolution during the molding is remarkably prevented.

This application is based on a patent application (Japanese Patent Application No. Hei 11-273462) filed in Japan, the content of which is incorporated herein by reference.

#### BACKGROUND ART

An improvement in impact resistance of resin materials is industrial useful because it increases uses of materials and makes it possible to reduce the thickness of molded articles and to enlarge the size of them. Therefore, various methods for improving the impact resistance of the resin materials have been studied.

As the material whose impact resistance was enhanced by using a rubber polymer in combination with a rigid resin, for example, ABS resin, high-impact polystyrene resin, modified PPE resin and MBS resin-reinforced polyvinyl chloride resin have already been employed industrially.

In particular, as the resin material having good weather resistance, using a saturated rubber component such as alkyl (meth)acrylate rubber is employed as a rubber polymer, for example, an ASA resin as a weather resistible ABS resin has been suggested.

As the method of preventing pearled gloss (pearled gloss defective) of colored molded articles as a drawback of the ASA resin, for example, a method of using a multi-layer crosslinked acrylic rubber containing a diene rubber in particles is suggested in Japanese Patent Application, Second Publication No. Sho 47-47863 and Japanese Patent Application, Second Publication No. Sho 59-49245.

Furthermore, a method of improving moldability and a method of improving balance between the gloss and impact resistance are disclosed in Japanese Patent Application, Second Publication No. Hei 3-66329. This publication suggests to use a composite rubber graft copolymer which contains a diene rubber enlarged by an acid

group-containing copolymer latex in particles, and also has an outer-layer portion made of a crosslinked acrylate polymer obtained by using a graft-linking agent a crosslinking agent in combination.

Furthermore, Japanese Patent Application, First Publication No. Hei 10-77383 describes that a resin composition containing graft copolymer has good impact resistance by using a diene rubber which has a specific molecular weight of a toluene-soluble component, specific gel content and specific swell to toluene.

However, these prior arts do not describe with respect to gas evolution in case a resin composition containing a graft copolymer is molded, and gloss of molding in case molding conditions such as molding temperature are changed. The resin composition containing the graft copolymer prepared by the method of the Examples had the following problems. That is, a large amount of the gas is generated when the composition is molten and molded at comparatively high temperature and the gas adheres to the mold or resin surface, thereby to cause poor appearance such as poor gloss of the resulting molded article, and to be likely to make the working environment worse during molding. Although a technique of lowering a molding temperature, i.e. resin temperature, is generally employed to prevent the molding gas from evolving, it makes impossible to obtain a large-size or complicated resin molded article because of lack of fluidity of the resin.

That is, these resin compositions of the prior art had such drawbacks that they are hardly employed as raw materials of various molded articles because of very narrow molding conditions capable of maintaining the operation environment during the molding at good state and improving design of the resulting molded articles.

Therefore, there has not hitherto been found out any material which prevents the molding gas from evolving under wide molding temperature conditions and has good gloss of molding in the resin composition containing an alkyl (meth)acrylate rubber, and it has been requested strongly to develop a technique which meets these requirements.

#### DISCLOSURE OF THE INVENTION

An object of the present invention is to provide a thermoplastic resin composition which prevents a gas from evolving during the molding on wide molding temperature conditions and exhibits good gloss of molding, and also has excellent weather resistance, impact resistance and fluidity.

The present inventors have intensively studied about the fluidity of a resin composition containing a specific graft copolymer as well as the amount of a gas evolved during the molding at high temperature. Surprisingly, they have found that a resin composition, which contains a specific graft copolymer and contains an emulsifier residue in a specific range, has good fluidity and causes less gas evolution during the molding at high temperature, thus accomplishing the present invention.

That is, the graft copolymer (G) of the present invention is a graft copolymer which is prepared by emulsion graft polymerization of a rubber polymer comprising 0-50% by weight of a butadiene unit and 50-100% by weight of a (meth)acrylate unit and at least one monomer selected from aromatic alkenyl compound, methacrylate, acrylate and vinyl cyanide compound, said graft copolymer containing 0.5-2.0% by weight of an emulsifier residue.

#### BEST MODE FOR CARRYING OUT THE INVENTION

The present invention will be described in detail below.

The rubber polymer which constitutes the graft copolymer (G) of the present invention comprises 0-50% by weight of a butadiene unit and 50-100% by weight of a (meth)acrylate unit. When the proportion of the butadiene unit in the rubber polymer exceeds 50% by weight, the weather resistance of the resulting thermoplastic resin composition containing the graft copolymer (G) is lowered, which is not preferable.

The butadiene unit is a polymer composed of a diene unit such as 1,3-butadiene or isoprene and, if necessary, a monomer unit capable of copolymerizing with the diene unit.

As the (meth)acrylate, for example, there can be preferably used alkyl acrylate such as methyl acrylate, ethyl acrylate, n-propyl acrylate, n-butyl acrylate, or 2-ethylhexyl acrylate; and alkyl methacrylate such as hexyl methacrylate, 2-ethylhexyl methacrylate, or n-lauryl methacrylate. Particularly, N-butyl acrylate is preferably employed.

The rubber polymer is an alkyl (meth)acrylate homopolymer, or a copolymer containing a butadiene unit and a (meth)acrylate unit, or a composite rubber polymer of a butadiene polymer and a (meth)acrylate polymer.

When employing the copolymer containing a butadiene unit and a (meth)acrylate unit, the copolymer is preferably employed after enlarging by an inorganic acid, an inorganic salt or an acid group-containing copolymer latex because of excellent impact

resistance of the thermoplastic resin composition containing the graft copolymer (G).

When employing the composite rubber polymer of a butadiene polymer and a (meth)acrylate polymer, it is preferably to employ after enlarging the butadiene polymer using at least one enlarging agent selected from inorganic acid, inorganic salt, organic acid, inorganic acid anhydride and acid group-containing copolymer latex to a particle diameter within a range of 200-500 nm, followed by emulsion polymerization of the (meth)acrylate component in the presence of this enlarged butadiene polymer latex. When employing such a composite rubber polymer, the impact resistance of the thermoplastic resin composition containing the graft copolymer (G) is excellent and the pigmentation also becomes superior.

The acid group-containing copolymer latex employed as the enlarging agent is a copolymer latex having an acid group-containing unit and an alkyl acrylate unit and is known to Japanese Patent No. 1,146,549 and Japanese Patent No. 1,556,865. The acid group-containing monomer includes, for example, acrylic acid, methacrylic acid, itaconic acid, or crotonic acid, while an alkyl acrylate having 1-12 carbon atoms is preferable as the alkyl acrylate. The proportion of the acid group-containing monomer in the acid group-containing copolymer is within a range of 3-30% by weight, and more preferably within a range of 10-25% by weight, based on the copolymer, because the stability of the latex is excellent in case of particle-enlarging of the butadiene polymer and the average particle diameter of the resulting enlarged butadiene polymer is easily controlled within a range of 200-500 nm. The weight-average particle diameter of the acid group-containing copolymer in the acid group-containing copolymer latex is preferably within a range of 100-200 nm because the stability of the latex is excellent in case of particle-enlarging of the butadiene polymer and the average particle diameter of the resulting enlarged butadiene polymer is easily controlled within a range of 200-500 nm.

The particle-enlarging can be performed by adding the above acid group-containing copolymer latex to the butadiene polymer latex having a particle diameter of 150 nm or less prepared by the emulsion polymerization.

The lower limit of the weight-average particle diameter of the enlarged butadiene polymer is 200 nm, preferably 300 nm, and more preferably 350 nm. On the other hand, the upper limit is 500 nm, preferably 450 nm, and more preferably 400 nm. When the weight-average particle diameter is within the above range, the impact resistance of the resulting thermoplastic resin composition tends to be excellent.

In case of the emulsion polymerization of a (meth)acrylate component in the presence of an enlarged butadiene polymer having a particle diameter within a range of 200-500 nm, when employing a graft-linking agent and/or a crosslinking agent in combination with the (meth)acrylate, the impact resistance and pigmentation of the thermoplastic resin composition containing the graft copolymer (G) are improved, which is preferable.

Examples of the graft-linking agent employed together with the (meth)acrylate include allyl methacrylate, triallyl cyanurate, triallyl isocyanurate and the like. Examples of the crosslinking agent include ethylene glycol dimethacrylate, propylene glycol dimethacrylate, 1,3-butylene glycol dimethacrylate, 1,4-butylene glycol dimethacrylate and the like.

The method of emulsion polymerization of the (meth)acrylate component in the presence of the butadiene polymer latex is not specifically limited and examples thereof include a method of polymerizing by adding a (meth)acrylate monomer mixture containing a crosslinking agent and/or a graft-linking agent to a butadiene polymer latex in a single portion, a method of polymerizing by intermittently adding a (meth)acrylate monomer mixture to a butadiene polymer latex in two or more portions, and a method of continuously adding dropwise a (meth)acrylate monomer mixture to a butadiene polymer latex while polymerizing the (meth)acrylate monomer mixture. Among these methods, the method of polymerizing by adding in a single portion is preferable in view of the impact resistance.

When employing a composite rubber polymer as the rubber polymer in the graft copolymer (G), the lower limit of the amount of the butadiene polymer is preferably 1% by weight, more preferably 5% by weight, and still more preferably 10% by weight, based on 100% by weight of the composite rubber polymer. On the other hand, the upper limit is preferably 50% by weight, more preferably 40% by weight, and still more preferably 30% by weight, based on 100% by weight of the composite rubber polymer. When the amount of the butadiene polymer is within the above range, balance between the weather resistance and impact resistance is excellent.

The lower limit of the weight-average particle diameter of the rubber polymer thus obtained is preferably 200 nm, more preferably 250 nm, and still more preferably 300 nm. On the other hand, the upper limit is preferably 500 nm, more preferably 450 nm, and still more preferably 400 nm. When the weight-average particle diameter of the

rubber polymer is within the above range, the impact resistance and pigmentation of the resulting thermoplastic resin composition are excellent.

With respect to the particle size distribution of the rubber polymer, the lower limit of the proportion of particles having a particle diameter of less than 100 nm in the rubber polymer is preferably 1% by weight, more preferably 3% by weight, and still more preferably 5% by weight, because the gloss and impact resistance during the molding at high temperature of the thermoplastic resin composition containing the graft copolymer (G) are excellent. On the other hand, the upper limit is preferably 30% by weight, more preferably 25% by weight, and still more preferably 20% by weight. The method of controlling the particle size distribution of the rubber polymer is not specifically limited and examples thereof include a method of mixing a rubber polymer having a particle diameter of 100 nm or more and a rubber polymer having a particle diameter less than 100 nm, which have been previously prepared, and a method of employing a specific amount of an emulsifier in the preparation of the rubber polymer. Among these methods, the method of employing a specific amount of an emulsifier is preferable because of its simple preparation process. More preferable method is a method of preparing a rubber polymer by the emulsion polymerization method employing an emulsifier having a small molecule occupy area.

The molecule occupy area of the emulsifier employed is within a range of 10-50  $\text{\AA}^2$ , and preferably within a range of 10-40  $\text{\AA}^2$ . When employing the emulsifier having such a molecule occupy area, particles having a particle diameter less than 100 nm are formed in the polymerization of the rubber polymer, resulting in preferable particle size distribution.

Examples of the emulsifier having such a molecule occupy area include sodium or potassium salts of fatty acids such as oleic acid, stearic acid, myristic acid, stearic acid, and palmitic acid, sodium lauryl sulfate, sodium N-lauroyl sarcosinate, dipotassium alkenylsuccinate, sodium alkyl diphenyl ether disulfonate, and the like. When employing an acid type emulsifier having two or more functional groups in a molecule or a salt thereof among these emulsifiers, gas evolution can be prevented during the molding of the thermoplastic resin composition, which is preferable. Among these, the dipotassium alkenylsuccinate or sodium alkyl diphenyl ether disulfonate is preferable. The dipotassium alkenylsuccinate is more preferable because the rubber polymer can be easily recovered from the latex by coagulating using sulfuric acid. Examples of the

dipotassium alkenylsuccinate include dipotassium octadecenylsuccinate, dipotassium heptadecenylsuccinate, dipotassium hexadecenylsuccinate and the like. In this case, other emulsifiers may also be used in combination in the amount of less than 50% by weight based on the amount of the total emulsifier.

The graft copolymer (G) of the present invention is obtained by the emulsion polymerization of the above rubber polymer and at least one monomer selected from aromatic alkenyl compound, methacrylate, acrylate and vinyl cyanide compound in the presence of the emulsifier.

Examples of the aromatic alkenyl compound include styrene,  $\alpha$ -methylstyrene, vinyltoluene and the like. Examples of the methacrylate include methyl methacrylate, ethyl methacrylate, 2-ethylhexyl methacrylate and the like. Examples of the acrylate include methyl acrylate, ethyl acrylate, n-butyl acrylate and the like. Examples of the vinyl cyanide compound include acrylonitrile, methacrylonitrile and the like. Among these monomers, a mixture of styrene and acrylonitrile is preferable because of excellent thermal stability of the graft copolymer (G).

In this case, the amount of the monomer is not specifically limited but the lower limit of the amount of the monomer is preferably 40 parts by weight, more preferably 50 parts by weight, and still more preferably 60 parts by weight, based on 100 parts by weight of the rubber polymer, because the impact resistance and pigmentation of the thermoplastic resin composition containing the graft copolymer (G) are excellent. On the other hand, the upper limit of the amount of the monomer is preferably 200 parts by weight, more preferably 180 parts by weight, and still more preferably 150 parts by weight, based on 100 parts by weight of the rubber polymer.

The emulsion graft polymerization for preparation of the graft copolymer (G) can be performed by adding at least one selected from aromatic alkenyl compound, methacrylate, acrylate and vinyl cyanide compound to a rubber polymer latex in the presence of an emulsifier, using a conventional radical polymerization technique. Various conventional chain transfer agents can be added in the monomer in order to control the graft ratio and molecular weight of the graft component.

As the radical polymerization initiator, for example, a peroxide, an azo initiator, or a redox initiator employing an oxidizing agent in combination with a reducing agent may be employed. Among these initiators, the redox initiator is preferable and a sulfoxylate initiator employing ferrous sulfate, sodium ethylenediaminetetraacetate,

Rongalite and hydroperoxide in combination is particularly preferable.

As the emulsifier, the emulsifier employed in the preparation of the above rubber polymer may be employed as it is and not added before the graft polymerization process, or may be added, if necessary. The emulsifier is not specifically limited, but there can be employed various carboxylates such as dipotassium alkenylsuccinate, sodium alkyldiphenyl ether disulfonate, sodium N-lauroylsuccinate, fatty acid potassium, fatty acid sodium, and rosin soap because the stability of the latex is excellent during the emulsion polymerization and the graft ratio is liable to be enhanced.

The graft copolymer (G) can be recovered by pouring the graft copolymer (G) latex thus prepared into hot water in which a coagulant is dissolved, followed by coagulation and further solidification. As the coagulant, for example, an inorganic acid such as sulfuric acid, hydrochloric acid, phosphoric acid or nitric acid, or a metal salt such as calcium chloride, calcium acetate or aluminum sulfate can be employed. Among these, an inorganic acid is preferably employed as the coagulant because the productivity of the graft copolymer (G) is excellent and the thermal coloration can be prevented during the molding of the thermoplastic resin composition containing the same.

The graft copolymer (G) of the present invention can be obtained by redispersing the graft copolymer (G) recovered by the above method in water or warm water to form a slurry, and washing the slurry thereby to elute an emulsifier residue and a coagulant remained in the graft copolymer (G), followed by recovery in a dehydrator and further drying in an air-dryer.

The amount of the emulsifier residue in the graft copolymer (G) varies depending on the amount of the emulsifier and the conditions of the washing treatment of the graft copolymer (G).

The graft copolymer (G) of the present invention contains the emulsifier residue and the lower limit of the emulsifier residue is 0.5% by weight, while the upper limit of the emulsifier residue is 2% by weight. The lower limit is preferably 1.0% by weight, while the upper limit is preferably 1.5% by weight. In order to adjust to such an amount of the emulsifier residue, control of the amount of the emulsifier or the step of controlling the conditions of the washing treatment of the graft copolymer (G) is required. When the amount of the emulsifier residue in the graft copolymer (G) is adjusted to the above range by this step, the fluidity and gas evolution during the molding of the resulting thermoplastic resin composition become superior.



Regarding the graft copolymer (G), 1% weight loss temperature on the measurement of TG-DTA under the conditions of 20°C /minute is preferably 300°C or higher, and more preferably 310°C or higher. When the 1% weight loss temperature is 300°C or higher, the molding gas evolution during the molding at high temperature of the thermoplastic resin containing the graft copolymer (G) tends to decrease.

Although the graft copolymer (G) may be employed alone, the thermoplastic resin composition of the present invention can be prepared by mixing the other thermoplastic resin (F) with the graft copolymer (G) and optionally kneading the mixture together with the other graft copolymer (S) using a conventional kneader. The amount of the graft copolymer (G) is within a range of 1-100% by weight based on 100% by weight of the thermoplastic resin composition. The amount of the other graft copolymer (S) is within a range of 99-0% by weight based on 100% by weight of the thermoplastic resin composition. The amount of the other thermoplastic resin (F) is within a range of 99-0% by weight based on 100% by weight of the thermoplastic resin composition.

The other graft copolymer (S) is at least one selected from ABS resin (S-1), ethylene-propylene-non-conjugated diene rubber graft copolymer (S-2) and polyorganosiloxane/(meth)acrylate composite rubber graft copolymer (S-3).

As the ABS resin (S-1), a conventional resin can be employed is obtained by grafting a butadiene rubber with a polymer having at least one unit selected from aromatic alkenyl unit, vinyl cyanide unit and (meth)acrylate unit.

The ethylene-propylene-non-conjugated diene rubber graft copolymer (S-2) is obtained by grafting an EPDM (ethylene-propylene-non-conjugated diene rubber elastic material) with a polymer having at least one unit selected from aromatic alkenyl unit, (meth) acrylate unit and vinyl cyanide unit. EPDM is preferably EPDM in which a weight ratio of ethylene to propylene is within a range from 80:20 to 30:70 and the amount of the non-conjugated diene such as dicyclopentadiene, alkylidenenorbornene or 1,4-hexanediene is within a range of 0.5-30% by mole. Examples of the aromatic alkenyl compound among the monomers employed in the preparation of the ethylene-propylene-non-conjugated diene rubber graft copolymer (S-2) include styrene,  $\alpha$ -methylstyrene, vinyltoluene and the like. Examples of the methacrylate include methyl methacrylate, ethyl methacrylate, 2-ethylhexyl methacrylate and the like. Examples of the acrylate include methyl acrylate, ethyl acrylate, n-butyl acrylate and the like. Examples of the vinyl cyanide compound include acrylonitrile, methacrylonitrile and the

like. Among these monomers, a mixture of styrene and acrylonitrile is preferable because of excellent thermal stability of the resulting ethylene-propylene-non-conjugated diene rubber graft copolymer (S-2). Typical products of the ethylene-propylene-non-conjugated diene rubber graft copolymer (S-2) obtained by the graft polymerization of EPDM and the mixture of styrene and acrylonitrile, i.e. AES resin, are "W220" manufactured by Techno Polymer Co. and "UNIBRIGHT 500" manufactured by Nippon A&L Co., Ltd., which are commercially available. The method of the graft polymerization of EPDM and the monomer is a conventional method such as solution, bulk, bulk-suspension or emulsion polymerization method.

The polyorganosiloxane/(meth)acrylate composite rubber graft copolymer (S-3) is obtained by the graft polymerization of a composite rubber polymer of polyorganosiloxane and a (meth)acrylate polymer, and at least one monomer selected from aromatic alkenyl compound, methacrylate, acrylate and vinyl cyanide compound.

The polyorganosiloxane is not specifically limited, but is preferably polyorganosiloxane having a vinyl group. More preferably, it is polyorganosiloxane comprising 0.3-3% by mole of a vinyl group-containing siloxane and 97-99.7% by mole of a dimethylsiloxane unit, the proportion of a silicon atom having three or more siloxane bonds is 1% by mole or less based on the total silicon atoms in polydimethylsiloxane.

The dimethylsiloxane employed in the preparation of the polyorganosiloxane includes a cyclic dimethylsiloxane with a 3- or poly-membered ring, preferably 3- to 7-membered ring. Specific examples thereof include hexamethylcyclotrisiloxane, octamethylcyclotetrasiloxane, decamethylcyclopentasiloxane, dodecamethylcyclohexasiloxane and the like, and these are used alone or in combination.

The vinyl group-containing siloxane has a vinyl group and is capable of bonding with dimethylsiloxane through a siloxane bond, and various alkoxysilane compounds having a vinyl group are preferable in view of the reactivity with dimethylsiloxane.

Specific examples thereof include methacryloyloxysiloxane such as

$\beta$ -methacryloyloxyethyltrimethoxymethylsilane,

$\gamma$ -methacryloyloxypropyltrimethoxymethylsilane,

$\gamma$ -methacryloyloxypropylmethoxydimethylsilane,

$\gamma$ -methacryloyloxypropyltrimethoxysilane,  $\gamma$ -methacryloyloxypropylethoxydiethylsilane,

$\gamma$ -methacryloyloxypropyldiethoxymethylsilane, and

$\delta$ -methacryloyloxybutyldiethoxymethylsilane; vinylsiloxane such as

tetramethyltetravinylcyclotetrasiloxane; and mercaptosiloxane such as p-vinylphenyldimethoxymethylsilane,  $\gamma$ -mercaptopropyldimethoxymethylsilane, and  $\gamma$ -mercaptopropyltrimethoxysilane. These vinyl group-containing siloxanes can be employed alone or in combination.

In order to prepare polyorganosiloxane, first, a siloxane crosslinking agent is optionally added to a siloxane mixture of dimethylsiloxane and vinyl group-containing siloxane and the mixture is emulsified by an emulsifier and water to obtain a latex. Then, the resulting latex is formed into fine particles by using a homomixer for forming into fine particles by a shear force due to high-speed rotation or a homogenizer for forming into fine particles by an ejection force due to a high pressure generator. When employing a high-pressure emulsification device such as homogenizer, the particle size distribution of the polyorganosiloxane latex is lowered, which is preferable. The latex formed into fine particles is added in an aqueous acid solution containing an acid catalyst, and then polymerized at high temperature. The polymerization reaction is terminated by cooling the reaction solution and further neutralizing with an alkali substance such as caustic soda, caustic potash, sodium carbonate or the like.

As the siloxane crosslinking agent, for example, trifunctional or tetrafunctional silane crosslinking agent such as trimethoxymethylsilane, triethoxyphenylsilane, tetramethoxysilane, tetraethoxysilane, tetrabutoxysilane, or the like can be employed.

The emulsifier is preferably an anionic emulsifier and, for example, an emulsifier selected from sodium alkylbenzenesulfonate and sodium polyoxyethylene nonyl phenyl ether sulfate is employed. Among these emulsifiers, a sulfonic acid emulsifier such as sodium alkylbenzenesulfonate, sodium lauryl sulfonate, or the like is preferable. These emulsifiers are employed in the amount within a range of about 0.05-5 parts by weight based on 100 parts by weight of the siloxane mixture.

Examples of the acid catalyst employed in the polymerization of polyorganosiloxane include sulfonic acids such as aliphatic sulfonic acid, aliphatic substituted benzenesulfonic acid and aliphatic substituted naphthalenesulfonic acid; and mineral acids such as sulfuric acid, hydrochloric acid and nitric acid. These acid catalysts can be employed alone or in combination. Among these acid catalysts, aliphatic substituted benzenesulfonic acid is preferable because of excellent stabilization effect of the polyorganosiloxane latex, and n-dodecylbenzenesulfonic acid is particularly preferable. When employing n-dodecylbenzenesulfonic acid in combination with the

A mixture of the (meth)acrylate, crosslinking agent and/or graft-linking agent is added in a latex of polyorganosiloxane and the mixture is polymerized by using a conventional radical polymerization initiator to prepare a composite of organosiloxane and a (meth)acrylate polymer. The mixture may be mixed with the polyorganosiloxane latex

in a single portion, or may be added dropwise in the polyorganosiloxane latex at a fixed rate. However, the method of mixing with the polyorganosiloxane latex in a single portion is preferable because the impact resistance of the finally obtainable thermoplastic resin composition is excellent.

As the radical polymerization initiator employed in the polymerization, for example, a peroxide, an azo initiator, or a redox initiator employing an oxidizing agent in combination with a reducing agent may be employed. Among these initiators, the redox initiator is preferable and a sulfoxylate initiator employing ferrous sulfate, sodium ethylenediaminetetraacetate, Rongalite, and hydroperoxide in combination is particularly preferable.

In the graft copolymer (S-3), the amount of the graft component obtained by the graft copolymerization of at least one monomer selected from aromatic alkenyl compound, methacrylate, acrylate and vinyl cyanide compound is within a range of 40-80% by weight based on the total amount (100% by weight) of the polyorganosiloxane/(meth)acrylate composite polymer.

When the amount is less than 40% by weight, the pigmentation of the thermoplastic resin composition molded article containing the graft copolymer (S-3) tends to be lowered. On the other hand, when the amount exceeds 80% by weight, the amount of the polyorganosiloxane/(meth)acrylate composite polymer is reduced and, therefore, the impact resistance is liable to be lowered. In view of both of the pigmentation and impact resistance, the amount is preferably within a range of 50-70% by weight, and more preferably within a range of 50-60% by weight.

Examples of the aromatic alkenyl compound employed in the graft component include styrene,  $\alpha$ -methylstyrene, vinyltoluene and the like. Examples of the methacrylate include methyl methacrylate, ethyl methacrylate, 2-ethylhexyl methacrylate and the like. Examples of the acrylate include methyl acrylate, ethyl acrylate, n-butyl acrylate and the like. Examples of the vinyl cyanide compound include acrylonitrile, methacrylonitrile and the like. Among these monomers, a mixture of styrene and acrylonitrile is preferable in view of thermal stability of the thermoplastic resin composition containing the graft copolymer (G).

The other thermoplastic resin (F) is not specifically limited and examples thereof include methyl polymethacrylate, acrylonitrile-styrene copolymer (AS resin), acrylonitrile-styrene-N-substituted maleimide terpolymer, styrene-maleic anhydride

copolymer, styrene-maleic anhydride-N-substituted maleimide terpolymer, polycarbonate resin, polybutylene terephthalate (PBT resin), polyethylene terephthalate resin (PET resin), polyvinyl chloride; polyolefin such as polyethylene, polypropylene; styrene elastomer such as styrene-butadiene-styrene (SBS), styrene-butadiene (SBR), hydrogenated SBS, and styrene-isoprene-styrene (SIS); various olefin elastomers; various polyester elastomers; polystyrene, methyl methacrylate-styrene copolymer (MS resin), acrylonitrile-styrene-methyl methacrylate copolymer, polyacetal resin, modified polyphenylene ether (modified PPE resin), ethylene-vinyl acetate copolymer, PPS resin, PES resin, PEEK resin, polyarylate, liquid crystal polyester resin, and polyamide resin (nylon). These thermoplastic resins can be used alone in combination thereof.

In the present invention, 5-40 parts by weight of a bromine flame retardant, 0.1-20 parts by weight of an antimony compound and 1-40 parts by weight of a phosphorous flame retardant can be further mixed with 100 parts by weight of the thermoplastic resin composition comprising 1-100% by weight of the graft copolymer (G), 99-0% by weight of the other graft copolymer (S) and 99-0% by weight of the other thermoplastic resin (F) for the purpose of providing the thermoplastic resin composition with the flame retardancy.

The bromine flame retardant is not specifically limited and a conventional one can be employed. For example, there can be preferably employed tetrabromobisphenol A and a derivative thereof, tetrabromobisphenol S, tetrabromophthalic anhydride, hexabromobenzene, brominated diphenyl ether, brominated polycarbonate oligomer and a terminal modified product thereof, brominated epoxy resin (bisphenol A type, novolak type) and a terminal modified product thereof, brominated phenoxy resin, trisbromophenyl phosphate, brominated polystyrene, and brominated phenylene ether oligomer. The bromine flame retardant is preferably a bromine flame retardant in which the bromine content is 10% by weight or more, and more preferably within a range of about 40-85% by weight, though it depends on types of the bromine flame retardant to be employed. When employing such a bromine flame retardant, the thermoplastic resin composition is provided with high flame retardancy, which is preferable. The higher the bromine content, the more the bromine flame retardant can provide the thermoplastic resin composition with the flame retardancy using a small amount of the bromine flame retardant without impairing physical properties of the thermoplastic resin other than the flame retardancy.

The amount of the bromine flame retardant is usually within a range of 5-40 parts by weight, and preferably within a range of 10-35 parts by weight, based on 100 parts by weight of the thermoplastic resin composition, though it depends on the degree of the flame retardancy to be required. When the amount is less than 5 parts by weight, the effect of providing the thermoplastic resin with the flame retardancy becomes poor. On the other hand, when the amount exceeds 40 parts by weight, the impact resistance and heat resistance of the thermoplastic resin composition are lowered.

The antimony compound can be added to further improve the flame retardancy of the thermoplastic resin composition, and various antimony compounds can be employed. Examples thereof include antimony trioxide, antimony pentaoxide, and antimonate such as sodium antimonate. As these antimony compounds, surface-treated antimony compounds are commercially available and may be employed.

The amount of the antimony compound is within a range of 0.1-20% by weight based on 100 parts by weight of the thermoplastic resin composition comprising 1-100% by weight of the graft copolymer (G), 99-0% by weight of the other graft copolymer (S) and 99-0% by weight of the other thermoplastic resin (F). When the amount exceeds 20 parts by weight, the impact resistance of the finally obtainable thermoplastic resin composition is lowered sometimes. On the other hand, when the amount is less than 0.1 parts by weight, an improvement in flame retardancy due to the antimony compound becomes insufficient sometimes.

The phosphorous flame retardant employed in the present invention is not specifically limited and a conventional one can be employed. Examples thereof include monophosphate such as trimethyl phosphate, triethyl phosphate, tributyl phosphate, trioctyl phosphate, tributoxyethyl phosphate, triphenyl phosphate, trixyl phosphate, tricresyl phosphate, cresylphenyl phosphate, xyldiphenyl phosphate, octyldiphenyl phosphate, diisopropylphenyl phosphate, tris(chloroethyl) phosphate, diphenyl methylphosphate, diethyl phenylphosphate, and resorcinyldiphenylphosphate; phenylenebis (diphenylphosphate) such as bisphenol A bisphosphate, hydroquinone-bisphosphate, and dihydroxybiphenyl-bisphosphate; polyphosphate such as phenylenebis(dixylylphosphate), phenylenebis(ditolyldiphenylphosphate), bisphenol A-bis(diphenylphosphate), bisphenol A-bis(dixylylphosphate), bisphenol A-bis(ditolyldiphenylphosphate), biphenylenebis(diphenylphosphate), biphenylenebis(dixylylphosphate), and biphenylenebis(ditolyldiphenylphosphate); and inorganic

compound such as polyphosphoric acid and red phosphorous. Preferably, monophosphate, phenylenebis(diphenylphosphate) or red phosphorous is employed. These phosphorous flame retardants can be employed alone or in combination.

The amount of the phosphorous flame retardant is usually within a range of 1-40 parts by weight, and preferably within a range of 2-30 parts by weight based on 100 parts by weight of the thermoplastic resin composition comprising 1-100% by weight of the graft copolymer (G), 99-0% by weight of the other graft copolymer (S) and 99-0% by weight of the other thermoplastic resin (F), though it depends on the degree of the flame retardancy to be required and types of the phosphorous compound. When the amount is less than 1 part by weight, the effect of providing the thermoplastic resin composition with the flame retardancy becomes poor. On the other hand, when the amount exceeds 30 parts by weight, the impact resistance and heat resistance are lowered. In this case, 0-20 parts by weight of the bromine flame retardancy is preferably employed in combination with 1-40 parts by weight of the phosphorous flame retardant.

For the purpose of further improving the flame retardancy, at least one auxiliary flame retardant selected from polytetrafluoroethylene, chlorinated polyethylene and silicone oil may be incorporated into the thermoplastic resin composition.

The composition of the polytetrafluoroethylene is not specifically limited and a conventional one can be employed, but polytetrafluoroethylene having a molecular weight of 1,000,000 or more is preferable. When the molecular weight of the polytetrafluoroethylene is less than 1,000,000, a large amount of the above flame retardant is required to meet high flame retardancy, e.g. UL 94 Standard (Under Writers Laboratories Inc., USA) test. As a result, the moldability and the mechanical strength of the finally obtainable thermoplastic resin composition are lowered sometimes.

Types of the chlorinated polyethylene are not specifically limited and a conventional one can be employed. A chlorinated polyethylene whose chlorine content is within a range of 20-70% by weight is preferable and a chlorinated polyethylene whose chlorine content is within a range of 30-50% by weight is more preferable.

Examples of the silicone oil include polydimethylsiloxane, polymethylphenylsiloxane, polymethylhydrodienesiloxane and the like. There can also be employed a modified silicone oil obtained by epoxy modification, alkyl modification, amino modification, carboxyl modification and alcohol modification of an alkyl group of a polydialkylsiloxane in which the number of the carbon of the alkyl group is usually within



a range of 1-18. The viscosity of the silicone oil is usually within a range of 1-10000 cSt at a temperature of 25°C, preferably within a range of 5-5000 cSt, and more preferably within a range of 5-2000 cSt. When the viscosity is less than 1 cSt, the desired effect of improving the flame retardancy is poor. On the other hand, when the viscosity exceeds 10000 cSt, the compatibility with the resin is lowered.

The polytetrafluoroethylene, chlorinated polyethylene and silicone oil may be used alone or in combination, and are incorporated in the total amount within a range of 0.0001-5 parts by weight based on 100 parts by weight of the thermoplastic resin composition comprising 1-100% by weight of the graft copolymer (G), 99-0% by weight of the other graft copolymer (S) and 99-0% by weight of the other thermoplastic resin (F). When the amount is less than 0.0001 parts by weight, drip during the combustion is liable to occur, that is, it tends to become insufficient to provide with high flame retardancy. On the other hand, when the amount exceeds 5 parts by weight, the moldability as well as appearance, heat resistance and impact resistance of the molded article tend to be lowered. When employing the silicone oil, the silicone oil breeds out on the surface of the resin sometimes. When employing the silicone oil alone, the amount is preferably within a range of 0.005-2 parts by weight based on 100 parts by weight of the thermoplastic resin composition.

These auxiliary flame retardants may be added alone or in combination with the chlorinated polyethylene or silicone oil. Preferably, polytetrafluoroethylene is preferably employed alone because the polytetrafluoroethylene is superior in effect of improving the flame retardancy to the chlorinated polyethylene or silicone oil.

For the purpose of further enhancing the stiffness and lowering the linear expansion coefficient, an inorganic filler can be incorporated into the thermoplastic resin composition. Examples of the inorganic filler, which can be added, include one or more inorganic fillers such as glass fiber, carbon fiber, wollastonite, talc, mica, glass foil, and potassium titanate. The amount of the inorganic filler is preferably within a range of 1-50 parts by weight, and more preferably within a range of 5-40 parts by weight, based on 100 parts by weight of the thermoplastic resin composition comprising 1-100% by weight of the graft copolymer (G), 99-0% by weight of the other graft copolymer (S) and 99-0% by weight of the other thermoplastic resin (F). When the inorganic filler is incorporated in the amount within the above range, the thermoplastic resin composition is superior in balance between the impact resistance, moldability and stiffness.

The thermoplastic resin composition of the present invention can be prepared, for example, by the method of weighing each predetermined amount of a powdered, beads-like or pelletized thermoplastic resin (F), a graft copolymer (G) and other graft copolymer (S), mixing them, and melting and kneading the mixture. In case of melting and kneading, a kneader such as Banbury mixer, pressure kneader, roll or the like is employed. The graft copolymer (G) and the thermoplastic resin composition containing the same can be fed as raw materials of the molded article as they are. If necessary, dyes, pigments, stabilizers, reinforcing fillers, flame retardants, blowing agents, lubricants, plasticizers, and antistatic agents can be incorporated into the thermoplastic resin composition. A desired molded article can be obtained from the graft copolymer (G) and the thermoplastic resin composition containing the same by various molding methods such as injection molding method, extrusion molding method, blow molding method, compression molding method, calendaring method, inflation molding and the like.

The thermoplastic resin composition containing the graft copolymer (G) of the present invention can be used in various molded articles and examples of industrial uses thereof include vehicle parts; building material parts such as exterior and interior parts, wall material, and window channeling which are used without being coated; dish and toy; electric appliances such as cleaner housing, television housing, and air-conditioner housing; interior members; vessel members and communications equipment housing; and electric appliance housings such as housing for note type personal computer, PDA housing, and housing for liquid crystal projector.

#### Examples

The following Examples and Comparative Examples further illustrate the present invention in detail but are not to be construed to limit the scope thereof unless they do not depart the gist thereof.

In the following Examples, percentages and parts are by weight unless otherwise stated. Various physical properties in the following Examples and Comparative Examples were determined by the following procedures.

(1) Weight-average particle diameter and weight proportion of particles having a particle diameter of less than 100 nm of rubber polymer in latex.

They were measured by using a submicron particle size distribution measuring device "CHDF-2000" manufactured by MATEC APPLIED SCIENCES.

After heating to the inner temperature of 50°C, an aqueous solution of 0.5 parts of sodium pyrophosphate, 0.005 parts of ferrous sulfate heptahydrate and 5 parts of water were added and the polymerization was initiated. A mixture of 68.6 parts of 1,3-butadiene and 3.6 parts of styrene was added dropwise at the polymerization temperature of 57°C by using a pressure pump. Then, 0.3 parts of normal dodecylmercaptan was added at the point of time at which the polymerization conversion

ratio reached 40%, and the polymerization was continued furthermore. After eight hours, the remained 1,3-butadiene was removed to obtain a butadiene polymer latex (B-1) having a solid content of 40.2%, a polymerization conversion rate of 97% and a weight-average particle diameter of 70 nm.

[Reference Example 2: Preparation of acid group-containing copolymer (K-1) for particle-enlarging]

The following respective components were charged in a glass reaction vessel equipped with a reagent injecting container, a cooling tube, a jacket heater and a stirrer (hereinafter abbreviated to a glass reaction vessel) and then heated to the inner temperature of 65°C while stirring.

Potassium oleate	2.2 Parts
Sodium dioctylsulfosuccinate	2.5 Parts
Sodium formaldehyde sulfoxylate dihydrate	0.3 Parts
Ferrous sulfate heptahydrate	0.003 Parts
Disodium ethylenediaminetetraacetate	0.009 Parts
Deionized water	200 Parts

To the mixed solution, a mixture of 81.5 parts of n-butyl acrylate, 18.5 parts of methacrylic acid and 0.5 parts of cumene hydroperoxide was added dropwise over two hours. Even after the completion of the dropwise addition, the polymerization was continued at the same temperature for two hours. Consequently, an acid group-containing copolymer latex for particle-enlarging (K-1) having a polymerization conversion rate of 98% and a weight-average particle diameter of 150 nm was obtained. [Reference Example 3: Preparation of acid group-containing copolymer (K-2) for particle-enlarging]

In the same manner as in the preparation of the acid group-containing polymer (K-1) for particle-enlarging of Reference Example 2, except that the amount of n-butyl acrylate was replaced by 85.0 parts of n-butyl and the amount of methacrylic acid was replaced by 15.0 parts, an acid group-containing copolymer latex for particle-enlarging (K-2) having a weight-average particle diameter of 120 nm was prepared.

[Reference Example 4: Preparation of acid group-containing copolymer (K-3) for particle-enlarging]

In the same manner as in the preparation of the acid group-containing polymer (K-1) for particle-enlarging of Reference Example 2, except that the amount of n-butylacrylate was replaced by 79.0 parts of n-butyl and the amount of methacrylic acid was replaced by 21.0 parts, an acid group-containing copolymer latex for particle-enlarging (K-3) having a weight-average particle diameter of 165 nm was prepared.

[Example 1: Preparation of graft copolymer (G-1)]

To 100 parts of the butadiene polymer latex (B-1, solid content) prepared in Reference Example 1, 2.1 parts of acid group-containing copolymer (K-1) for particle-enlarging prepared in Reference Example 2 (as solid content) was added while stirring at room temperature, followed by continuous stirring for additional 30 minutes to obtain an enlarged butadiene polymer latex. The weight-average particle diameter of the butadiene polymer after particle-enlarging was 380 nm.

In a glass reaction vessel, 10 parts of an enlarged butadiene polymer latex (as solid content), 0.3 parts of dipotassium alkenylsuccinate ("LATEMUL ASK" manufactured by Kao Corp., as actual amount, same rule applies correspondingly to the followings) and 175 parts of water (including water in the enlarged butadiene polymer latex) were charged. Under stirring, 40 parts of n-butyl acrylate, 0.16 parts of allyl methacrylate, a mixture of 0.08 parts of 1,3-butylene glycol dimethacrylate and 0.1 parts of tertiary butyl hydroperoxide was then added.

The atmosphere was replaced by nitrogen by passing a nitrogen flow through the reaction vessel, and then heated to 60°C. At the point of time at which the liquid temperature in the reaction vessel reached 50°C, an aqueous solution of 0.00015 parts of ferrous sulfate heptahydrate, 0.00045 parts of disodium ethylenediaminetetraacetate, 0.24 parts of Rongalite and 5.0 parts of water was added and the inner temperature was raised to 75°C, thereby initiating the radical polymerization. This state was maintained for one hour, thereby completing the polymerization of the acrylate component to obtain a latex of a composite rubber polymer of an enlarged butadiene polymer and a n-butyl acrylate rubber. The weight-average particle diameter measured by using a small amount of this composite rubber polymer latex sampled was 300 nm and the proportion of the particles having a particle diameter of 100 nm or less was 8% based on the total weight.

An aqueous solution of 0.15 parts of Rongalite, 0.65 parts of dipotassium alkenylsuccinate and 10 parts of water was added, and then a mixed solution of 6.3 parts

of acrylonitrile, 18.7 parts of styrene and 0.11 parts of tertiary butyl hydroperoxide was added dropwise over one hour and the mixed solution was polymerized. After five minutes have been passed since the completion of the dropwise addition, an aqueous solution prepared from 0.001 parts of ferrous sulfate heptahydrate, 0.003 parts of disodium ethylenediaminetetraacetate, 0.15 parts of Rongalite and 5 parts of water was added and a mixed solution of 6.3 parts of acrylonitrile, 18.7 parts of styrene, 0.19 parts of tertiary butyl hydroperoxide and 0.014 parts of normal octylmercaptan was added dropwise over one hour and the mixed solution was polymerized. After the completion of the dropwise addition, the state at a temperature of 75°C was maintained for 10 minutes, followed by cooling. At the point of time at which the inner temperature reached 60°C, a dispersion of 0.2 parts of an antioxidant ("ANTAGE W500", manufactured by Kawaguchi Chemical Industries Co., Ltd.), 0.2 parts of dipotassium alkenylsuccinate and 5 parts of water was added. The above operation gave a latex of a graft copolymer obtained by graft copolymerization of a composite rubber polymer of an enlarged butadiene polymer and a n-butyl acrylate rubber, and acrylonitrile/styrene.

Then, the above polymer latex was charged in a 1.2-fold amount of an aqueous 0.6% sulfuric acid solution heated to 45°C while stirring, thereby coagulate a polymer. After the liquid temperature was raised to 65°C and maintained for five minutes, the liquid temperature was raised to 90°C. The coagulum was separated, and then the recovered product was subjected to a washing treatment by charging in a 10-fold amount of water and stirring for 10 minutes. This dispersion was dehydrated in a centrifugal drier and then dried at 80°C for 16 hours to obtain a graft copolymer (G-1).

The measurement results of the amount of the emulsifier residue in the graft copolymer (G-1) and those of 1% weight loss obtained by measuring TG-DTA under the conditions of 20°C /minute are shown in Table 1.

#### [Example 2: Preparation of graft copolymer (G-2)]

In the same manner as in the procedure for preparation of the graft copolymer (G-1) of Example 1, except that the amount of dipotassium alkenylsuccinate to be added together with the enlarged butadiene polymer latex was changed to 0.9 parts from 0.3 parts and the amount of dipotassium alkenylsuccinate to be added to the composite rubber polymer latex was changed to 0.05 parts from 0.65 parts, a graft copolymer (G-2) was prepared.

The measurement results of the amount of the emulsifier residue in the graft

copolymer (G-2) and those of 1% weight loss obtained by measuring TG-DTA under the conditions of 20°C /minute are shown in Table 1.

[Example 3: Preparation of graft copolymer (G-3)]

In the same manner as in the procedure for preparation of the graft copolymer (G-1) of Example 1, except that the amount of dipotassium alkenylsuccinate to be added together with the enlarged butadiene polymer latex was changed to 0 parts from 0.3 parts and the amount of dipotassium alkenylsuccinate to be added to the composite rubber polymer latex was changed to 0.95 parts from 0.65 parts, a graft copolymer (G-3) was prepared. The results are shown in Table 1.

The measurement results of the amount of the emulsifier residue in the graft copolymer (G-3) and those of 1% weight loss obtained by measuring TG-DTA under the conditions of 20°C /minute are shown in Table 1.

[Example 4: Preparation of graft copolymer (G-4)]

In the same manner as in the procedure for preparation of the graft copolymer (G-1) of Example 1, except that the acid group-containing copolymer latex (K-1) was replaced by (K-2), a graft copolymer (G-4) was prepared.

The measurement results of the amount of the emulsifier residue in the graft copolymer (G-4) and those of 1% weight loss obtained by measuring TG-DTA under the conditions of 20°C /minute are shown in Table 1.

[Example 5: Preparation of graft copolymer (G-5)]

In the same manner as in the procedure for preparation of the graft copolymer (G-1) of Example 1, except that the acid group-containing copolymer latex (K-1) was replaced by (K-3), a graft copolymer (G-5) was prepared.

The measurement results of the amount of the emulsifier residue in the graft copolymer (G-5) and those of 1% weight loss obtained by measuring TG-DTA under the conditions of 20°C /minute are shown in Table 1.

[Example 6: Preparation of graft copolymer (G-6)]

In the same manner as in the procedure for preparation of the graft copolymer (G-1) of Example 1, except that the amount of the enlarged butadiene polymer was changed to 5 parts (solid content) and each amount of n-butyl acrylate, allyl methacrylate and 1,3-butylene glycol dimethacrylate, which constitute the acrylic rubber, is changed to 45 parts, 0.18 parts and 0.1 parts, respectively, a graft copolymer (G-6) was prepared.

The measurement results of the amount of the emulsifier residue in the graft

copolymer (G-6) and those of 1% weight loss obtained by measuring TG-DTA under the conditions of 20°C /minute are shown in Table 1.

[Example 7: Preparation of graft copolymer (G-7)]

In the same manner as in the procedure for preparation of the graft copolymer (G-1) of Example 1, except that the amount of the enlarged butadiene polymer was changed to 20 parts (solid content) and each amount of n-butyl acrylate, allyl methacrylate and 1,3-butylene glycol dimethacrylate, which constitute the acrylic rubber, is changed to 30 parts, 0.12 parts and 0.06 parts, respectively, a graft copolymer (G-7) was prepared.

The measurement results of the amount of the emulsifier residue in the graft copolymer (G-7) and those of 1% weight loss obtained by measuring TG-DTA under the conditions of 20°C /minute are shown in Table 1.

[Comparative Example 1: Preparation of graft copolymer (H-1)]

In the same manner as in the procedure for preparation of the graft copolymer (G-1) of Example 1, except that the amount of dipotassium alkenylsuccinate to be added to the composite rubber polymer latex was changed to 2.0 parts from 0.65 parts, a graft copolymer (H-1) was prepared.

The measurement results of the amount of the emulsifier residue in the graft copolymer (H-1) and those of 1% weight loss obtained by measuring TG-DTA under the conditions of 20°C /minute are shown in Table 1.

[Comparative Example 2: Preparation of graft copolymer (H-2)]

In the same manner as in the procedure for preparation of the graft copolymer (G-1) of Example 1, except that the amount of dipotassium alkenylsuccinate to be added to the composite rubber polymer latex was changed to 0.05 parts from 0.65 parts, a graft copolymer (H-2) was prepared.

The measurement results of the amount of the emulsifier residue in the graft copolymer (H-2) and those of 1% weight loss obtained by measuring TG-DTA under the conditions of 20°C /minute are shown in Table 1.



[Table 1]

	Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Example 7	Comp. Example 1	Comp. Example 2
Types of graft copolymer	G-1	G-2	G-3	G-4	G-5	G-6	G-7	H-1	H-2
Weight-average particle diameter of butadiene polymer after particle-enlarging (nm)	380	380	380	330	420	380	380	380	380
Proportion of butadiene component (% by weight)	20	20	20	20	20	10	40	20	20
Weight-average particle diameter (nm)	300	285	327	334	310	278	330	300	300
Proportion of particles having a particle diameter less than 100 nm (% by weight)	8	21	3	6	12	16	4	9	11
Parts*1 of emulsifier relative to graft copolymer (G)	① (parts by weight)	0.3	0.9	0.3	0.3	0.3	0.3	0.3	0.3
	② (parts by weight)	0.65	0.05	0.65	0.65	0.65	0.65	2.0	0.05
	③ (parts by weight)	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Amount of emulsifier residue (% by weight)	1.3	1.5	1.4	1.4	1.3	1.2	1.7	2.3	0.4
1% weight loss temperature (°C)	320	319	321	322	316	316	309	273	330

①: added before preparation of composite rubber polymer

②: added after preparation of composite rubber polymer

③: added after cooling

\*1: Parts relative to 100 parts by weight of graft copolymer

[Reference Example 5] Preparation of ABS resin (S-1)

In a glass reaction vessel, 48.9 parts of a butadiene polymer latex (B-1, as a solid content) was charged (at room temperature), and then 1.1 parts of an acid group-containing copolymer latex (K-2, solid content) was charged under stirring. Subsequently, the mixture was stirred at room temperature for 60 minutes to obtain an enlarged butadiene rubber polymer latex having a weight-average particle diameter of 330 nm and a solid content of 39.9%.

To this enlarged butadiene rubber polymer latex, 140 parts of water (including water contained in the rubber polymer latex), 0.6 parts of fructose, 0.01 parts of sodium phosphoric anhydride, 0.005 parts of ferrous sulfate heptahydrate and 0.1 parts of sodium hydroxide were added, and then the atmosphere was replaced by nitrogen under stirring and heated to 50°C. To the mixture, a mixture of 15 parts of acrylonitrile, 35 parts of styrene, 0.5 parts of t-dodecylmercaptan and 0.3 parts of cumene hydroperoxide was added dropwise over 180 minutes and the inner temperature was controlled so that it does not exceed 65°C during the dropwise addition. After the completion of the dropwise addition, 0.12 parts of cumene hydroperoxide was added and, furthermore, the mixture was maintained for one hour and cooled. To the resulting latex, 1 part of an antioxidant ("ANTAGE W400", manufactured by Kawaguchi Chemical Industries Co., Ltd.) was added and the latex was poured into an aqueous 1.2% sulfuric acid solution (70°C) in the same amount as that of this graft polymer latex, thereby to cause coagulation. A butadiene graft polymer (ABS resin, S-1) was obtained as a milk white powder by heating to 90°C and maintaining for five minutes, followed by dehydration, washing and further drying.

[Reference Example 6: Ethylene-propylene-non-conjugated diene rubber graft copolymer]

As an ethylene-propylene-non-conjugated diene rubber graft copolymer, an AES resin "W220" manufactured by Techno Polymer Co. was employed.

[Reference Example 7: Preparation of polyorganosiloxane (L-1)]

98 Parts of octamethylcyclotetrasiloxane and 2 parts of  $\gamma$ -methacryloyloxypropyldimethoxymethylsilane were mixed to obtain 100 parts of a siloxane mixture. To the siloxane mixture, a solution prepared by dissolving 0.67 parts of sodium dodecylbenzenesulfonate in 300 parts of deionized water was added and, after stirring in a homomixer at 10000 rpm for two minutes, the mixture was once passed through a homogenizer at a pressure of 200 kg/cm<sup>2</sup> to obtain a stable premixed

organosiloxane latex.

On the other hand, in a reaction vessel equipped with a reagent injecting container, a cooling tube, a jacket heater and a stirrer, 10 parts of dodecylbenzenesulfonic acid and 90 parts of water were charged to prepare an aqueous 10% dodecylbenzenesulfonic acid solution.

In the state where this aqueous solution is heated to 85°C, the premixed organosiloxane latex was added dropwise over four hours. After the completion of the dropwise addition, the temperature was maintained for one hour and then lowered. Then, the reaction product was neutralized by adjusting the pH to 7 using an aqueous sodium hydroxide solution.

The polyorganosiloxane (L-1) latex thus obtained was dried at 170°C for 30 minutes and the solid content was determined. As a result, it was 17.7%. The weight-average particle diameter of the polyorganosiloxane (L-1) in the latex was 50 nm. [Reference Example 8: Preparation of graft copolymer (S-3a)]

In a glass reaction vessel, 8.0 parts of the polyorganosiloxane (L-1) latex (solid content) prepared in Reference Example 7, 0.2 parts of "EMAL NC-35" (polyoxyethylene alkyl phenyl ether sulfate, manufactured by Kao Corp.) and 200 parts of water were mixed, and then a mixture of 42 parts of n-butyl acrylate, 0.3 parts of allyl methacrylate, 0.1 parts of 1,3-butylene glycol dimethacrylate and 0.11 parts of t-butyl hydroperoxide was added.

The atmosphere was replaced by nitrogen by passing a nitrogen flow through this reaction vessel while stirring, and then heated to 60°C. At the point of time at which the liquid temperature in the reaction vessel reached 60°C, an aqueous solution of 0.000075 parts of ferrous sulfate, 0.000225 parts of disodium ethylenediaminetetraacetate, 0.2 parts of Rongalite and 10 parts of water was added, thereby initiating the radical polymerization. The liquid temperature was raised to 78°C by the polymerization of the acrylate component. This state was maintained for one hour, thereby completing the polymerization of the acrylate component to obtain a latex of a composite rubber polymer of an polyorganosiloxane and a n-butyl acrylate rubber.

After the liquid temperature in the reaction vessel was lowered to 70°C, an aqueous solution of 0.25 parts of Rongalite and 10 parts of water was added, and then a mixed solution of 2.5 parts of acrylonitrile, 7.5 parts of styrene and 0.05 parts of t-butyl hydroperoxide was added dropwise over two hours and the mixed solution was polymerized. After the completion of the dropwise addition, the state at a temperature of

60°C was maintained for one hour and an aqueous solution of 0.001 parts of ferrous sulfate, 0.003 parts of disodium ethylenediaminetetraacetate, 0.2 parts of Rongalite, 0.2 parts of "EMAL NC-35" (manufactured by Kao Corp.) and 10 parts of water was added and a mixed solution of 10 parts of acrylonitrile, 30 parts of styrene and 0.2 parts of t-butyl hydroperoxide was added dropwise over two hours and the mixed solution was polymerized. After the completion of the dropwise addition, the state at a temperature of 60°C was maintained for 0.5 hours and 0.05 parts of cumene hydroperoxide was added. Furthermore, the state at a temperature of 60°C was maintained for 0.5 hours, followed by cooling. To this latex, 0.5 parts of dipotassium alkenylsuccinate was added to obtain a latex of a graft copolymer (S-3a) obtained by graft copolymerization of a composite rubber polymer of polyorganosiloxane (L-1) and a n-butyl acrylate rubber, and acrylonitrile/styrene.

Then, 150 parts of an aqueous solution prepared by dissolving calcium acetate in a proportion of 1% was heated to 60°C and stirred. In this solution, 100 parts of a latex of a graft copolymer (S-3a) was added dropwise, gradually, thereby coagulate the solution. The deposit was separated, washed, and then dehydrated for two minutes, and then dried over 24 hours at a temperature of 85°C to obtain a graft copolymer (S-3a).

[Reference 9: Preparation of polyorganosiloxane (L-2) latex]

97.5 Parts of octamethylcyclotetrasiloxane, 0.5 parts of  $\gamma$ -methacryloyloxypropyldimethoxymethylsilane and 2 parts of tetraethoxysilane were mixed to obtain 100 parts of a siloxane mixture. To the siloxane mixture, an aqueous solution of 1 part of dodecylbenzenesulfonic acid, 1 part of sodium dodecylbenzenesulfonate and 200 parts of water was added and, after stirring in a homomixer at 10000 rpm for two minutes, the mixture was once passed through a homogenizer at a pressure of 200 kg/cm<sup>2</sup> to obtain a stable premixed organosiloxane latex.

This premixed organosiloxane latex was charged in a glass reaction vessel, heated at 80°C for five hours while mixing with stirring, cooled to about 20°C, and then allowed to stand for 48 hours. The reaction product was neutralized by adjusting the pH to 7 using an aqueous caustic soda solution, thereby completing the polymerization.

The polyorganosiloxane (L-2) latex thus obtained was dried at 170°C for 30 minutes and the solid content was determined. As a result, it was 36.5%. The weight-average particle diameter of the polyorganosiloxane (L-2) in the latex was 160 nm.

[Reference Example 10: Preparation of graft copolymer (S-3b)]

In a reaction vessel equipped with a reagent injecting container, a cooling tube, a jacket heater and a stirrer, 30 parts of the polyorganosiloxane (L-2) latex (solid content) prepared in Reference Example 6 and 295 parts of water were mixed. After the atmosphere was replaced by nitrogen and heated to 50°C, a mixture of 37.5 parts of n-butyl acrylate, 2.5 parts of allyl methacrylate and 0.3 parts of t-butyl hydroperoxide was added, followed by stirring at room temperature for 30 minutes. Then, an aqueous solution of 0.0003 parts of ferrous sulfate pentahydrate, 0.001 parts of disodium ethylenediaminetetraacetate, 0.17 parts of Rongalite and 5 parts of deionized water was added, thereby initiating the radical polymerization. The polymerization was maintained at the inner temperature of 70°C for two hours, thereby completing the polymerization of the acrylate component to obtain a latex of a composite rubber polymer. This latex was partially collected and the weight-average particle diameter of the composite rubber polymer was measured. As a result, it was 190 nm.

To this composite rubber polymer latex, a mixture of 9 parts of acrylonitrile, 21 parts of styrene and 0.3 parts of t-butyl hydroperoxide was added dropwise at the inner temperature of 70°C over 45 minutes. Then, this state was maintained at 70°C for four hours, thereby completing the graft polymerization.

This graft copolymer (S-3b) latex was charged in the same amount an aqueous calcium chloride solution at 60°C while stirring, and then coagulated by maintaining at 80°C for five minutes, then at 95°C for five minutes. The deposit was separated, washed, centrifuged and then dried at 85°C for 24 hours to obtain a graft copolymer (S-3b).

[Reference Example 11: Preparation of other thermoplastic resin (F-1)]

An acrylonitrile-styrene copolymer (F-1) comprising 29 parts of acrylonitrile and 71 parts of styrene, in which a reducing viscosity measured in a N,N-dimethylformamide solution at 25°C is 0.60 dl/g, was prepared by a conventional suspension polymerization method.

[Reference Example 12: Preparation of other thermoplastic resin (F-2)]

An acrylonitrile-styrene-N-phenylmaleimide terpolymer (F-2) comprising 20 parts of acrylonitrile, 53 parts of styrene and 27 parts of N-phenylmaleimide, in which a reducing viscosity measured in a N,N-dimethylformamide solution at 25°C is 0.65 dl/g, was prepared by a conventional continuous solution polymerization method.

[Reference Example 13: Preparation of other thermoplastic resin (F-3)]

An acrylonitrile-styrene-glycidyl methacrylate terpolymer (F-3) having an

epoxy group, comprising 25 parts of acrylonitrile, 74.6 parts of styrene and 0.4 parts of glycidyl methacrylate, in which a reducing viscosity measured in a N,N-dimethylformamide solution at 25°C is 0.50 dl/g, was prepared by a conventional suspension polymerization method.

[Reference Example 14: Preparation of other thermoplastic resin (F-4)]

An acrylonitrile-styrene-methyl methacrylate terpolymer (F-4) comprising 7 parts of acrylonitrile, 23 parts of styrene and 70 parts of methyl methacrylate, in which a reducing viscosity measured in a N,N-dimethylformamide solution at 25°C is 0.38 dl/g, was prepared by a conventional suspension polymerization method.

[Reference Example 15: Preparation of other thermoplastic resin (F-5)]

An acrylic resin (F-5) comprising 99 parts of methyl methacrylate and 1 part of methyl acrylate, in which a reducing viscosity measured in a N,N-dimethylformamide solution at 25°C is 0.25 dl/g, was prepared by a conventional suspension polymerization method.

[Reference Example 16: Preparation of other thermoplastic resins (F-6) to (F-9)]

As a polycarbonate resin (F-6), "IUPILON S2000F" manufactured by Mitsubishi Engineering-Plastics Corporation was employed. As a polyester resin (F-7), "TUFPET N1300" manufactured by Mitsubishi Rayon Co., Ltd. was employed. As an ultrahigh-molecular acrylic resin (F-8), "METABLEN P-531" manufactured by Mitsubishi Rayon Co., Ltd. was employed. As a vinyl chloride resin (F-9), "TK-1000" (polymerization degree: 1,000) manufactured by Shin-Etsu Chemical Co., Ltd. was employed.

[Examples 8 to 86 and Comparative Examples 3 to 27: Preparation of thermoplastic resin compositions and evaluation of performances]

The respective graft copolymers (G-1 to G-7, H-1 and H-2) prepared in Examples 1 to 7 and Comparative Examples 1 and 2 and, if necessary, other graft copolymers (S-1, 2, 3a and 3b), other thermoplastic resins (F-1 to F-9), 0.3 parts of "ADEKA STAB C" manufactured by Asahi Denka Kogyo K.K., 0.3 parts of barium stearate, 0.4 parts of ethylenebisstearylamine and 0.8 parts of carbon black ("#960", manufactured by Mitsubishi Chemical Corporation) were mixed by using a Henschel mixer and the resulting mixture was fed into an deaeration type extruder ("PCM-30", manufactured by Ikegai Tekko Corporation) heated to a temperature within a range of 230-260°C, and then kneaded to obtain pellets.

As the bromine flame retardant, one terminal-modified tetrabromo bisphenol A (“SR-T104N”, manufactured by Sakamoto Yakuhin Kogyo Co., Ltd.) was employed. As the antimony compound, antimony trioxide was employed. As the chlorinated polyethylene, “E-230” manufactured by Daiso Co., Ltd. was employed. As the polytetrafluoroethylene, “F201L” manufactured by Daikin Industries, Ltd. was employed. As the silicone oil, “SH-200” manufactured by Toray Dow Corning Co., Ltd. was employed. As the phosphorous flame retardant, triphenyl phosphate and red phosphorous were employed. As the glass fiber, “ECSO3T-34” manufactured by Nippon Electric Glass Co., Ltd. was employed. As the carbon fiber, “PYROFIL TR-06U” manufactured by Mitsubishi Rayon Co., Ltd. was employed. As the talc, “MICROTALC MP10-52” manufactured by Pfizer MSP K.K. was employed. As the wollastonite, “NYGROS8” manufactured by Tomoe Engineering Co., Ltd. was employed. As the mica, “WG325” manufactured by Hayashi Kasei, Ltd. was employed.

The evaluation results of MI, gloss of molding, pigmentation properties, Izod impact strength, Rockwell hardness, gas evolution during the molding, weather resistance, flame retardancy, short shot pressure, drawdown properties during the extrusion, and linear expansion coefficient, which were measured by using the resulting pellets, are shown in Tables 2 to 16.

These properties were evaluated by the following procedures.

#### (4) Melt flow rate (MI)

It was measured by the method defined in ASTM D1238 under the conditions of a barrel temperature of 200°C and a loading of 49 N or a barrel temperature of 220°C and a loading of 98 N.

#### (5) Gloss of thermoplastic resin composition

Using an injection molder “J85-ELII” manufactured by Nippon Seikosho Co., Ltd., a plate of 100 mm × 100 mm × 3 mm in size was molded under the conditions of a cylinder setting temperature of 230°C or 280°C, a mold temperature of 60°C and an injection speed of 50%. Gloss of the resulting molded plate was measured by using a gloss meter “GM-26D” manufactured by Murakami Shikisai Kenkyusho Co., Ltd.

#### (6) Evaluation of pigmentation of thermoplastic resin composition

Using an injection molder “J85-ELII” manufactured by Nippon Seikosho Co., Ltd., a plate of 100 mm × 100 mm × 3 mm in size was molded under the conditions of a cylinder setting temperature of 230°C, a mold temperature of 60°C and an injection speed

of 50%. Color hue of the resulting black-colored molded plate was measured (measurement of  $L^*$ ) by using a high-speed spectrophotometer "CMS-1500" manufactured by Murakami Shikisai Kenkyusho Co., Ltd. in accordance with JIS Z8729.

(7) Measurement of Izod impact test

It was measured by the method defined in ASTM D256. The Izod impact strength under a low temperature atmosphere was measured after leaving Izod specimens under an atmosphere at  $-30^{\circ}\text{C}$  for 12 hours or more.

(8) Measurement of surface hardness (Rockwell hardness)

It was measured by the method defined in ASTM D785.

(9) Evaluation of gas evolution during molding

Using an injection molder "J85-ELII" manufactured by Nippon Seikosho Co., Ltd., the amount of smoke evolved during the flow of a molten resin under the conditions of a cylinder setting temperature of  $280^{\circ}\text{C}$  and an injection speed of 50% was visually observed. Criteria for judgment are as follows.

○: Small amount of smoke

△: Medium amount of smoke

×: Large amount of smoke

(10) Evaluation of weather resistance

A white-colored plate of  $100\text{ mm} \times 100\text{ mm} \times 3\text{ mm}$  in size was treated by using a Sunshine Weather-Ometer (manufactured by Suga Test Instrument Co., Ltd.) at a black panel temperature of  $63^{\circ}\text{C}$  and cycle conditions of 60 minutes (rainfall: 12 minutes) for 600 hours. The results were evaluated by the degree of color change ( $\Delta E$ ) measured by a color difference meter.

(11) Short shot pressure

Using a horizontal molder "M-100" manufactured by Meiki Co., Ltd., a minimum pressure enough to mold into a plate of  $100\text{ mm} \times 100\text{ mm} \times 3\text{ mm}$  in size at a cylinder temperature of  $240^{\circ}\text{C}$  was indicated by percentage (%) based on a maximum pressure ( $2,000\text{ kgf/cm}^2$ ) as an index of the fluidity of the thermoplastic resin composition.

(12) Evaluation of flame retardancy

Using an injection molder "SAV-60" manufactured by Sanjo Seiki Co., Ltd., a test piece of 1/16 inch in thickness was made under the conditions of a cylinder setting temperature within a range of  $200\text{--}250^{\circ}\text{C}$  and a mold temperature of  $60^{\circ}\text{C}$ , and then the



drip initiation time was measured by continuously bringing this specimen closer to flame in accordance with a vertical test defined in UL-94 Standard until drip occurs, thus deciding UL-94 grade.

#### (13) Evaluation of drawdown

Using a 30 mm uniaxial extruder (“Laboplaskomill”, manufactured by Toyo Seiki Co., Ltd.) set at a barrel temperature of 210°C, a square bar was extruded at a screw speed of 30 rpm and then the resin’s deflection width between an extruder die and a sizing die was measured. Specimens where the amount is 1 mm or less were rated ○, while specimens where the amount is 1 mm or more were rated ×.

#### (14) Linear expansion coefficient

Using specimens obtained by cutting out the above square bar, it was measured by a thermomechanical analyzer “TMA-100” manufactured by Seiko Instruments Co., Ltd. Specimens where an average linear expansion coefficient at a temperature within a range of −30 to +60°C is  $6.5 \times 10^{-5}$  m/m/°C or less were rated ○, while specimens where an average linear expansion coefficient at a temperature within a range of −30 to +60°C exceeds  $6.5 \times 10^{-5}$  m/m/°C were rated ×.

[Table 2]

		Example 8	Example 9	Example 10	Example 11	Example 12	Example 13	Example 14
Graft copolymer(parts by weight)	(G)	G-1 48	G-2 48	G-3 48	G-4 48	G-5 48	G-6 48	G-7 48
	(H)							
	(S)							
Other thermoplastic resin (parts by weight)		52	52	52	52	52	52	52
MI*1			1.5	1.4	1.5	1.7	1.4	1.5
Gloss of molding	Molding at 230°C		92	91	91	89	92	90
	Molding at 280°C		80	50	83	81	69	66
Pigmentation (L*)		12.2	11.8	12.8	13.3	11.6	13.0	12.0
Izod strength*2	impact measured at 23°C	265	270	200	245	250	235	240
	measured at -30°C	90	92	75	73	91	72	96
Rockwell hardness (R scale)		94	92	94	93	92	93	93
Molding gas evolution (280°C)		○	○	○	○	○	○	○ - △
Weather resistance ΔE		2.4	2.6	2.1	2.8	2.0	1.6	3.8

\*1: MI was measured at 200°C under loading of 49 N (5 kgf)

\*2: Izod specimen has a thickness of 1/4 inch

[Table 3]

		Example 15	Example 16	Example 17	Example 18	Example 19	Comp. Example 3	Comp. Example 4
Graft copolymer(parts by weight)	(G)	G-1 36	G-1 24	G-1 36	G-1 24	G-1 30		
	(H)						H-1 48	H-1 48
	(S)	S-1 12	S-2 50	S-2 25	S-3a 24	S-3a 18		
Other thermoplastic resin (parts by weight)	(F-1)	52	26	39	52	52	52	52
MI*1		1.8	1.2	1.2	1.3	1.1	1.5	0.9
Gloss of molding	Molding at 230°C	93	80	90	95	95	92	92
	Molding at 280°C	84	68	75	69	73	38	81
Pigmentation (L*)		10.2	11.1	11.8	9.5	10.4	12.3	12.1
Izod impact strength*2	Measured at 23°C	320	298	285	330	300	260	255
	Measured at -30°C	111	135	120	68	95	89	88
Rockwell hardness (R scale)		93	93	94	93	94	94	94
Molding gas evolution (280°C)		○ - △	○ - △	○	○	○	×	○
Weather resistance ΔE		4.5	2.8	2.6	1.7	2.3	2.3	2.8

\*1: MI was measured at 200°C under loading of 49 N (5 kgf)

\*2: Izod specimen has a thickness of 1/4 inch

[Table 4]

		Example 20	Example 21	Example 22	Example 23	Example 24	Comp. Example 5	Comp. Example 6
Graft copolymer (parts by weight)	(G)	G-1 40	G-2 40	G-3 40	G-1 20	G-1 20		
	(H)						H-1 40	H-2 40
	(S)				S-3a 20	S-3b 20		
Other thermoplastic resin (parts by weight)	(F-1)	17	17	17	17	17	17	17
	(F-2)	43	43	43	43	43	43	43
MI*1		3.6	3.4	3.5	4.1	3.3	3.3	2.1
Izod impact	measured at 23°C	105	110	95	110	125	100	115
strength*2	measured at -30°C	66	63	58	70	55	62	68
Molding gas evolution(280°C)		○	○	○	○	○	×	○

\*1: MI was measured at 220°C under loading of 98 N (10 kgf)

\*2: Izod specimen has a thickness of 1/4 inch

[Table 5]

		Example 25	Example 26	Example 27	Example 28	Example 29	Comp. Example 7	Comp. Example 8
Graft copolymer (parts by weight)	(G)	G-1 40	G-2 40	G-3 40	G-1 20	G-1 20		
	(H)						H-1 40	H-2 40
	(S)				S-3a 20	S-3b 20		
Other thermoplastic resin (parts by weight)	(F-4)	60	60	60	60	60	60	60
MI*1		6.2	6.1	6.3	6.1	6.0	6.9	4.8
Izod impact	measured at 23°C	135	120	145	130	160	125	140
strength*2	measured at -30°C	63	61	63	63	58	60	64
Molding gas evolution (280°C)		○	○	○	○	○	×	○
Weather resistance ΔE		1.1	1.2	1.1	1.3	0.8	1.0	1.1

\*1: MI was measured at 230°C under loading of 37 N (3.8 kgf)

\*2: Izod specimen has a thickness of 1/4 inch

[Table 6]

	Example 30	Example 31	Example 32	Example 33	Example 34	Comp. Example 9	Comp. Example 10
Graft copolymer (parts by weight)	(G)	G-1 40	G-3 40	G-1 20	G-1 20		
	(H)					H-1 40	H-2 40
	(S)			S-3a 20	S-3b 20		
Other thermoplastic resin (parts by weight)	(F-5)	60	60	60	60	60	60
MI*1	(g/10 min)	2.3	2.2	2.4	2.3	2.1	1.6
Izod impact strength*2	measured at 23°C	115	105	120	110	120	120
	measured at -30°C	65	63	65	66	49	64
Molding gas evolution (280°C)		○	○	○	○ - △	○	○
Weather resistance ΔE		0.8	0.7	0.9	1.0	0.6	0.9

\*1: MI was measured at 230°C under loading of 37 N (3.8 kgf)

\*2: Izod specimen has a thickness of 1/4 inch

[Table 7]

		Example 34	Example 35	Example 36	Example 37	Example 38	Comp. Example 11	Comp. Example 12
Graft copolymer (parts by weight)	(G)	G-1 24	G-2 24	G-3 24	G-1 12	G-1 18		
	(H)						H-1 24	H-2 24
	(S)				S-3a 12	S-3b 6		
Other thermoplastic resin (parts by weight)	(F-1)	16	16	16	16	16	16	16
	(F-6)	60	60	60	60	60	60	60
	MI*1	7.7	7.4	7.8	7.3	7.5	7.3	5.2
Izod impact strength*2	measured at 23°C	630	650	590	725	760	620	635
	measured at -30°C	270	255	208	265	313	248	250
Molding gas evolution (280°C)		○	○	○	○	○	×	○

\*1: MI was measured at 220°C under loading of 98 N (10 kgf)

\*2: Izod specimen has a thickness of 1/4 inch

[Table 8]

		Example 39	Example 40	Example 41	Example 42	Comp. Example 13	Comp. Example 14
Graft copolymer (parts by weight)	(G)	G-1 46	G-2 46	G-3 46	G-1 23		
	(H)					H-1 46	H-1 46
	(S)				S-3a 23		
Other thermoplastic resin (parts by weight)	(F-1)	54	54	54	54	54	54
Bromine flame retardant (parts by weight)	SR-T104N	25	25	25	25	25	25
Antimony trioxide (parts by weight)		7	7	7	7	7	7
Chlorinate polyethylene (parts by weight)	E-230	2.5	2.5	2.5		2.5	2.5
Polytetrafluoroethylene (parts by weight)					0.1		
Silicone oil (parts by weight)		0.02	0.02	0.02	0.02	0.02	0.02
MI*1	(g/10 min)	3.8	3.7	3.4	3.4	3.6	2.8
Izod impact strength*2	measured at 23°C	118	120	105	110	116	110
	measured at -30°C	53	55	48	62	55	52
Flame retardancy [UL-94]		V-0	V-0	V-0	V-0	V-0	V-0
Molding gas evolution (250°C)		○	○	○	○	×	○

\*1: MI was measured at 200°C under loading of 49 N (5 kgf)

\*2: Izod specimen has a thickness of 1/4 inch



[Table 9]

	Example 43	Example 44	Example 45	Example 46	Example 47	Comp. Example 15	Comp. Example 16
Graft copolymer (parts by weight)	(G)	G-1 27	G-2 27	G-3 27	G-1 13.5	G-1 22	
	(H)						
	(S)				S-3a 13.5	S-3b 5	H-2 27
Other thermoplastic resin (parts by weight)	(F-1)	18	18	18	18	18	18
	(F-6)	55	55	55	55	55	55
Bromine flame retardant (parts by weight)	SR-T104N	15	15	15	15	15	15
Antimony trioxide(parts by weight)							
MI*1		5	5	5	5	5	5
Izod impact strength*2	measured at 23°C	9.5	9.1	9.2	9.0	9.3	7.3
	measured at -30°C	450	460	435	470	490	440
Flame retardancy [UL-94]		190	205	183	210	220	188
Molding gas evolution (250°C)		V-0	V-0	V-0	V-0	V-0	V-0
		○	○	○	○	○	○
						×	○

\*1: MI was measured at 220°C under loading of 98 N (10 kgf)

\*2: Izod specimen has a thickness of 1/4 inch

[Table 10]

		Example 48	Example 49	Example 50	Example 51	Example 52	Comp. Example 17
Graft copolymer (parts by weight)	(G)	G-1 20	G-2 20	G-3 20	G-1 10	G-1 10	
	(H)						H-1 20
	(S)				S-3a 10	S-3b 10	
Other thermoplastic resin (parts by weight)	(F-6)	80	80	80	80	80	80
Triphenyl phosphate (parts by weight)		15	15	15	15	15	15
MI*1	(g/10 min)	25.4	24.3	26.1	24.5	25.9	27.1
Izod impact strength *2	measured at 23°C	575	545	605	510	590	580
Flame retardancy [UL-94]		V-0	V-0	V-0	V-0	V-0	V-0
Molding gas evolution (250°C)		○ - △	○ - △	○ - △	○ - △	○ - △	×

\*1: MI was measured at 220°C under loading of 98 N (10 kgf)

\*2: Izod specimen has a thickness of 1/4 inch

[Table 11]

	Example 53	Example 54	Example 55	Example 56	Example 57	Comp. Example 18	Comp. Example 19
Graft copolymer (parts by weight)	(G)	G-1 32	G-2 32	G-3 32	G-1 16	G-1 26	
	(H)					H-1 32	H-2 32
	(S)				S-3a 16	S-3b 6	
Other thermoplastic resin (parts by weight)	(F-1)	28	28	28	28	28	28
	(F-6)	40	40	40	40	40	40
Bromine flame retardant (parts by weight)	SR-T104N	15	15	15	15	15	15
Antimony trioxide (parts by weight)		3	3	3	3	3	3
Filler	Carbon fiber	12	12	12	12	12	12
MI*1	(g/10 min)	2.4	2.5	2.3	2.2	2.5	2.4
Izod impact strength*2	measured at 23°C	90	92	88	92	96	89
	measured at -30°C	36	35	34	35	45	33
Flame retardancy [UL-94]		V-0	V-0	V-0	V-0	V-0	V-0
Molding gas evolution (250°C)		○	○	○	○	○	○
						×	○

\*1: MI was measured at 220°C under loading of 98 N (10 kgf)

\*2: Izod specimen has a thickness of 1/4 inch

[Table 12]

		Example 58	Example 59	Example 60	Example 61	Example 62	Comp. Example 20
Graft copolymer (parts by weight)	(G)	G-1 30	G-2 30	G-3 30	G-1 15	G-1 15	
	(H)						H-1 30
	(S)				S-3a 15	S-3b 15	
Other thermoplastic resin(parts by weight)	(F-1)	20	20	20	20	20	20
	(F-6)	40	40	40	40	40	40
	(F-7)	10	10	10	10	10	10
Red phosphorous(parts by weight)		5	5	5	5	5	5
MI*1		21.3	20.4	22.2	20.6	21.8	23.5
(g/10 min)							
Izod impact strength *2	measured at 23°C	180	170	185	170	180	175
Flame retardancy [UL-94]		V-0	V-0	V-0	V-0	V-0	V-0
Molding gas evolution (250°C)		○	○	○	○	○	×

\*1: MI was measured at 220°C under loading of 98 N (10 kgf)

\*2: Izod specimen has a thickness of 1/8 inch

[Table 13]

		Example 63	Example 64	Example 65	Example 66	Example 67	Comp. Example 21	Comp. Example 22
Graft copolymer (parts by weight)	(G)	G-1 25	G-2 25	G-3 25	G-1 13	G-1 13		
	(H)						H-1 25	H-2 25
	(S)				S-3a 12	S-3b 12		
Other thermoplastic resin (parts by weight)	(F-3)	15	15	15	15	15	15	15
	(F-7)	60	60	60	60	60	60	60
Izod impact strength * 1	(J/m)	550	510	585	525	605	560	565
Short shot pressure	%	28	27	28	29	27	26	31
Molding gas evolution (280°C)		○	○	○	○	○	×	○

\* 1: Izod specimen has a thickness of 1/4 inch

[Table 14]

		Example 68	Example 69	Example 70	Example 71	Example 72	Example 73	Example 74	Comp. Example 23
Graft copolymer (parts by weight)	(G)	G-1 25	G-1 25	G-1 25	G-2 25	G-3 25	G-1 13	G-1 13	
	(H)								H-1 25
	(S)						S-3a 12	S-3b 12	
Other thermoplastic resin (parts by weight)	(F-3)	15	15	15	15	15	15	15	15
	(F-7)	60	60	60	60	60	60	60	60
Filler	Glass fiber	35							
	Carbon fiber		30		30	30	30	30	30
	Talc			30					
Izod impact strength *1	measured at 23°C	195	225	160	180	210	185	210	215
Short shot pressure	%	35	36	34	35	34	36	35	33
Molding gas evolution (280°C)		○	○	○	○	○	○	○	×

\* 1: Izod specimen has a thickness of 1/4 inch

[Table 15]

		Example 75	Example 76	Example 77	Example 78	Example 79	Comp. Example 24	Comp. Example 25
Graft copolymer (parts by weight)	(G)	G-1 30	G-2 30	G-3 30	G-1 15	G-1 15		
	(H)						H-1 30	H-2 30
	(S)				S-3a 15	S-3b 15		
Other thermoplastic resin (parts by weight)	(F-3)	30	30	30	30	30	30	30
	(F-6)	20	20	20	20	20	20	20
	(F-7)	30	30	30	30	30	30	30
Izod impact	measured at 23°C	445	410	470	415	425	385	470
strength*1	measured at -30°C	196	188	203	201	221	173	205
Short shot pressure		27	26	27	28	27	25	30
Molding gas evolution (280°C)		○	○	○	○	○	×	○

\*1: Izod specimen has a thickness of 1/4 inch

$$\begin{aligned} & \frac{1}{\pi} \int_0^{2\pi} \frac{1}{1 - \cos \theta} d\theta = \frac{1}{\pi} \int_0^{2\pi} \frac{1}{1 - \cos \theta} d\theta = \frac{1}{\pi} \int_0^{2\pi} \frac{1}{1 - \cos \theta} d\theta = \frac{1}{\pi} \int_0^{2\pi} \frac{1}{1 - \cos \theta} d\theta = \frac{1}{\pi} \int_0^{2\pi} \frac{1}{1 - \cos \theta} d\theta \\ & \frac{1}{\pi} \int_0^{2\pi} \frac{1}{1 - \cos \theta} d\theta = \frac{1}{\pi} \int_0^{2\pi} \frac{1}{1 - \cos \theta} d\theta = \frac{1}{\pi} \int_0^{2\pi} \frac{1}{1 - \cos \theta} d\theta = \frac{1}{\pi} \int_0^{2\pi} \frac{1}{1 - \cos \theta} d\theta = \frac{1}{\pi} \int_0^{2\pi} \frac{1}{1 - \cos \theta} d\theta \end{aligned}$$
[illegible]



[Examples 87 to 91 and Comparative Example 28: Preparation of thermoplastic resin compositions]

10 Parts of the graft copolymers (G) prepared in Example 1 and the other graft copolymers (S) and (H) alone or in combination, 88 parts of the above vinyl chloride resin, 2 parts of the other thermoplastic resin(F-1), 1.5 parts of dibutyltin mercaptide ("T-17MJ", manufactured by Katsuda Kako Co., Ltd.) as the stabilizer, 1.2 parts of calcium stearate, 0.5 parts of glycerin monostearate ("RIKEMAL S-100A" manufactured by Riken Vitamin Co., Ltd.) and 5 parts of calcium carbonate as the filler were mixed using a Henschel mixer, and then pelletized by using a 30 mm  $\phi$  uniaxial extruder (L/D = 20) adjusted to a barrel temperature of 180°C. Furthermore, a square bar was extruded at a screw speed of 30 rpm by using a 30 mm  $\phi$  uniaxial extruder ("Laboplaskomill", manufactured by Toyo Seiki Co., Ltd.) adjusted to a barrel temperature of 190°C and the amount of a gas evolved was evaluated by the procedure described above. The resulting square bar was provided with a V-shaped notch and the Izod impact strength was determined. The results are shown in Table 17. In the table, the amount is represented by parts by weight.

[Table 17]

		Example 87	Example 88	Example 89	Example 90	Example 91	Comp. Example 28
Graft copolymer (parts by weight)	(G)	G-1 10	G-2 10	G-3 10	G-1 5	G-1 5	
	(H)						H-1 10
	(S)				S-3a 5	S-3b 5	
Other thermoplastic resin (parts by weight)	(F-1)	2	2	2	2	2	2
	(F-9)	88	88	88	88	88	88
Izod impact strength*1	measured at 23°C	330	295	340	1,360	1,450	310
	measured at -30°C	59	57	60	58	83	58
Molding gas evolution (190°C)		○	○	○	○	○	△ - ×

\*1: Izod specimen has a thickness of 1/4 inch

[Table 18]

	Other thermoplastic resin (F)	Extruder barrel setting temperature (°C)	Molder cylinder setting temperature (°C)	Molding gas evolution
Example 92	Polypropylene resin	200	220	○
Example 93	Polyethylene resin	200	220	○
Example 94	Polystyrene resin	200	220	○
Example 95	High-impact polystyrene resin	210	230	○
Example 96	Polyarylate resin	300	300	○ - △
Example 97	Liquid crystal polyester resin	350	350	○ - △
Example 98	Polyphenylene sulfide resin	350	350	○ - △
Example 99	6-nylon resin	280	280	○ - △
Example 100	6,6-nylon resin	300	300	○ - △
Example 101	Polyacetal resin	170	200	○
Example 102	Modified PPE resin	260	260	○
Example 103	Nylon/PPE alloy resin	290	290	○ - △

[Examples 92 to 103: Preparation of thermoplastic resin composition]

10 Parts of the graft copolymer(G-1) prepared in Example 1 and 90 parts of each thermoplastic resin shown in Table 18 were mixed by using a Henschel mixer, and then extruded under the conditions of the set barrel temperature shown in Table 18 to prepare thermoplastic resin composition pellets containing the graft copolymer (G-1). In the same manner, a plate of 100 mm × 100 mm in size was molded at the set cylinder temperature shown in Table 18, and the amount of a gas evolved was evaluated by the procedure described above.

In Table 18, the following resins were employed as the respective resins.

Polypropylene resin: “NOVATEC PP MA4” manufactured by Japan Polychem Co., Ltd.

Polyethylene resin: “NOVATEC LL UE320” manufactured by Japan Polychem Co., Ltd.

Polystyrene resin: “SUMIBRIGHT GP M140” manufactured by Sumitomo Chemical Industries Co., Ltd.

High-impact polystyrene resin: “SUMIBRIGHT H1 M540” manufactured by Sumitomo Chemical Industries Co., Ltd.

Polyarylate resin: “U POLYMER U-100” manufactured by Unitika Co., Ltd.

Liquid crystal polyester resin: “NOVACCULATE E335G30” manufactured by Mitsubishi Engineering-Plastics Corporation

Polyphenylene sulfide resin: “NOVAPPS 770R20” manufactured by Mitsubishi Engineering-Plastics Corporation

6-nlyon resin: “NOVAMID 1013C” manufactured by Mitsubishi Engineering-Plastics Corporation

6,6-nlyon resin: “NOVAMID 30100SR” manufactured by Mitsubishi Engineering-Plastics Corporation

Polyacetal resin: “DURACON M140” manufactured by Polyplastic Co., Ltd.

Modified polyphenylene ether (PPE) resin: “NORYL 731J” manufactured by Nippon GE Plastic Co., Ltd.

Nylon/PPE alloy resin: “NORYL GTX600” manufactured by Nippon GE Plastic Co., Ltd.

The followings are made apparent from the Examples and Comparative Examples.

(1) Any of the thermoplastic resin compositions (Example 8-43) containing the graft copolymers (G-1 to G-7) prepared in Examples 1 to 7 exhibited high fluidity and less molding gas evolution. Since the material, which exhibits high fluidity and causes less molding gas evolution, has excellent moldability on injection molding and has good pigmentation and weather resistance, its value in industrial use is very high.

(2) The thermoplastic resin composition containing the graft copolymer (G-1) of Example 8 exhibits high Izod impact strength and is superior in gloss of molding in case of molding at 280°C. On the other hand, the thermoplastic resin composition containing the graft copolymer (G-2) of Example 9 exhibits a tendency to slightly lower the gloss of the molded article obtained by molding at high temperature, while the thermoplastic resin composition containing the graft copolymer (G-3) of Example 10 exhibits a tendency to slightly lower the Izod impact strength.

(3) The thermoplastic resin composition containing the graft copolymer (H-1) prepared in Comparative Example 1 caused much gas evolution during the molding at high temperature. The thermoplastic resin composition, which causes much gas evolution during the molding, tend to make the working environment during the molding worse, or contaminate a mold with a volatile component during the injection molding thereby to cause corrosion of the mold. Therefore, its industrial value is low.

(4) The thermoplastic resin composition containing the graft copolymer (H-2) prepared in Comparative Example 2 exhibited poor fluidity because of low MI value or high short shot pressure. Regarding such a resin material, the injection molding conditions and the shape of the molded article are limited. Therefore, its industrial value is low.

### INDUSTRIAL APPLICABILITY

As described above, the thermoplastic resin composition, which contains a graft copolymer (G) containing a specific amount of an emulsifier residue of the present invention, is superior in impact resistance, fluidity and weather resistance and causes less gas evolution, and is also superior in molding appearance.

Its balance between high fluidity and small amount of a gas evolved during the molding is a very high level, which can not attained in case of a resin composition containing a graft copolymer which contains a conventionally known (meth)acrylate rubber as a constituent component. Accordingly, its value in use as various industrial

materials, especially weather-resistant material, is high.

The present invention may be embodied in other specific forms without departing from the spirit or essential characteristics thereof. The present embodiment is therefore to be considered in all respects as illustrative and not restrictive, the scope of the present invention being indicated by the appended claims rather than by the foregoing description and all changes which come within the meaning and range of equivalency of the claims are therefore intended to be embraced therein.

## CLAIMS

1. A graft copolymer (G) which is prepared by emulsion graft polymerization of a rubber polymer comprising 0-50% by weight of a butadiene unit and 50-100% by weight of a (meth)acrylate unit and at least one monomer selected from aromatic alkenyl compound, methacrylate, acrylate and vinyl cyanide compound, said graft copolymer containing 0.5-2.0% by weight of an emulsifier residue.
2. A graft copolymer (G) according to claim 1, wherein said rubber polymer is a composite rubber polymer obtained by emulsion polymerization of a (meth)acrylate component using a graft-linking agent and a crosslinking agent in combination in the presence of a butadiene polymer having a weight-average particle diameter within a range of 200-500 nm.
3. A graft copolymer (G) according to claim 2, wherein said butadiene polymer is enlarged by an acid group-containing copolymer latex.
4. A graft copolymer (G) according to claim 1, wherein said emulsifier residue is an acid type emulsifier having two or more functional groups in a molecule, or a salt thereof.
5. A graft copolymer (G) according to claim 4, wherein said acid type emulsifier having two or more functional groups in a molecule, or a salt thereof, is alkenylsuccinic acid or a salt thereof.
6. A graft copolymer (G) according to claim 1, wherein a 1% weight loss temperature on the measurement of TG-DTA under the conditions of 20°C/minute is 300°C or higher.
7. A graft copolymer (G) according to claim 1, wherein the amount of particles having a particle diameter less than 100 nm contained in the rubber polymer is within a range of 1-30% by weight.
8. A graft copolymer (G) according to claim 1, wherein the weight-average particle diameter of said rubber polymer is within a range of 200-500 nm.

9. A graft copolymer (G) according to claim 8, wherein the weight-average particle diameter of said rubber polymer is within a range of 250-450 nm.
10. A method of preparing a graft copolymer (G), which comprises performing emulsion graft polymerization of a rubber polymer comprising 0-50% by weight of a butadiene unit and 50-100% by weight of a (meth)acrylate unit and at least one monomer selected from aromatic alkenyl compound, methacrylate, acrylate and vinyl cyanide compound, said method comprising the step of controlling the amount of an emulsifier using so that the amount of an emulsifier residue in said graft copolymer is within a range of 0.5-2.0% by weight, or the step of controlling the conditions of a washing treatment of said graft copolymer.
11. A method of preparing a graft copolymer (G) according to claim 10, wherein said emulsifier residue is an acid type emulsifier having two or more functional groups in a molecule, or a salt thereof.
12. A method of preparing a graft copolymer (G) according to claim 11, wherein said emulsifier is an alkenylsuccinic acid or a salt thereof.
13. A thermoplastic resin composition comprising 1-100% by weight of the graft copolymer (G) of claim 1, 99-0% by weight of the other graft copolymer (S) and/or the other thermoplastic resin composition (F) (total of 100% by weight).
14. A thermoplastic resin composition according to claim 13, wherein said other thermoplastic resin composition (F) is at least one selected from the group consisting of acrylic resin, acrylonitrile-styrene (AS) resin, acrylonitrile-styrene-N-substituted maleimide terpolymer, styrene-maleic anhydride copolymer, styrene-maleic anhydride-N-substituted maleimide terpolymer, acrylonitrile-styrene-(meth)acrylate terpolymer, polyolefin resin, polyvinyl chloride resin, polystyrene resin, polyamide resin, polyester resin, polycarbonate resin, polyphenylene ether resin, polyacetal resin, polyarylate resin, polyphenylene sulfide resin, polyether ether ketone resin (PEEK resin), and polyether sulfone resin (PES resin).



15. A thermoplastic resin composition according to claim 13, wherein said other graft copolymer (S) is at least one selected from the group consisting of ABS resin (S-1), ethylene-propylene-non-conjugated diene rubber graft copolymer (S-2) and polyorganosiloxane/(meth)acrylate composite rubber graft copolymer (S-3).

16. A thermoplastic resin composition according to claim 13, further comprising 5-40 parts by weight of a bromine flame retardant and 0.1-20 parts by weight of an antimony compound, relative to 100 parts by weight of said thermoplastic resin composition.

17. A thermoplastic resin composition according to claim 13, further comprising 1-40 parts by weight of a phosphorous flame retardant and 0-20 parts by weight of a bromine flame retardant, relative to 100 parts by weight of said thermoplastic resin composition.

18. A thermoplastic resin composition according to claim 13, further comprising 0.0001-5 parts by weight of at least one auxiliary flame retardant selected from polytetrafluoroethylene, chlorinated polyethylene and silicone oil, based on 100 parts by weight of said thermoplastic resin composition.

19. A thermoplastic resin composition according to claim 13, further comprising 1-50 parts by weight of an inorganic filler, relative to 100 parts by weight of said thermoplastic resin composition.

20. A molded article which is prepared by molding said thermoplastic resin composition of claim 13.

21. A molded article according to claim 20, which is a housing for electric appliance or vehicle parts.

## ABSTRACT

The graft copolymer (G) of the present invention is a graft copolymer which is prepared by emulsion graft polymerization of a rubber polymer comprising 0-50% by weight of a butadiene unit and 50-100% by weight of a (meth)acrylate unit and at least one monomer selected from aromatic alkenyl compound, methacrylate, acrylate and vinyl cyanide compound, said graft copolymer containing 0.5-2.0% by weight of an emulsifier residue. The thermoplastic resin composition containing the graft copolymer of the present invention causes less gas evolution during the molding, provides a molded article with good gloss of molding, and has excellent weather resistance, impact resistance and fluidity.

## Declaration, Power Of Attorney and Petition

Page 1

WE (I) the undersigned inventor(s), hereby declare(s) that:

My residence, post office address and citizenship are as stated below next to my name,

We (I) believe that we are (I am) the original, first, and joint (sole) inventor(s) of the subject matter which is claimed and for which a patent is sought on the invention entitled

GRAFT COPOLYMER AND THERMOPLASTIC RESIN COMPOSITION CONTAINING THE GRAFT COPOLYMER

the specification of which

☐ is attached hereto.

☐ was filed on \_\_\_\_\_ as

Application Serial No. \_\_\_\_\_

and amended on \_\_\_\_\_.

☒ was filed as PCT international application

Number \_\_\_\_\_ PCT/JP00/06645

on \_\_\_\_\_ September 27, 2000

and was amended under PCT Article 19

on \_\_\_\_\_ (if applicable).

We (I) hereby state that we (I) have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

We (I) acknowledge the duty to disclose information known to be material to the patentability of this application as defined in Section 1.56 of Title 37 Code of Federal Regulations.

We (I) hereby claim foreign priority benefits under 35 U.S.C. § 119(a)-(d) or § 365(b) of any foreign application(s) for patent or inventor's certificate, or § 365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or PCT International application having a filing date before that of the application on which priority is claimed. Prior Foreign Application(s)

Application No.	Country	Day/Month/Year	Priority Claimed	
P11-273461	Japan	27/09/1999	<input type="checkbox"/> Yes	<input checked="" type="checkbox"/> No
P11-273462	Japan	27/09/1999	<input checked="" type="checkbox"/> Yes	<input type="checkbox"/> No
P11-342608	Japan	01/12/1999	<input type="checkbox"/> Yes	<input checked="" type="checkbox"/> No
P11-342609	Japan	01/12/1999	<input type="checkbox"/> Yes	<input checked="" type="checkbox"/> No
P11-342607	Japan	01/12/1999	<input type="checkbox"/> Yes	<input checked="" type="checkbox"/> No
P2000-010686	Japan	19/01/2000	<input type="checkbox"/> Yes	<input checked="" type="checkbox"/> No
			<input type="checkbox"/> Yes	<input type="checkbox"/> No
			<input type="checkbox"/> Yes	<input type="checkbox"/> No
			<input type="checkbox"/> Yes	<input type="checkbox"/> No
			<input type="checkbox"/> Yes	<input type="checkbox"/> No
			<input type="checkbox"/> Yes	<input type="checkbox"/> No
			<input type="checkbox"/> Yes	<input type="checkbox"/> No

We (I) hereby claim the benefit under Title 35, United States Code, § 119(e) of any United States provisional application(s) listed below.

_____	_____
(Application Number)	(Filing Date)
_____	_____
(Application Number)	(Filing Date)

We (I) hereby claim the benefit under 35 U.S.C. § 120 of any United States application(s), or § 365(c) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of 35 U.S.C. § 112, I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR § 1.56 which became available between the filing date of the prior application and the national or PCT International filing date of this application.

Application Serial No.	Filing Date	Status (pending, patented, abandoned)
_____	_____	_____
_____	_____	_____
_____	_____	_____

30 And we (I) hereby appoint: Norman F. Oblon, Reg. No. 24,618; Marvin J. Spivak, Reg. No. 24,913; C. Irvin McClelland, Reg. No. 21,124; Gregory J. Maier, Reg. No. 25,599; Arthur I. Neustadt, Reg. No. 24,854; Richard D. Kelly, Reg. No. 27,757; James D. Hamilton, Reg. No. 28,421; Eckhard H. Kuesters, Reg. No. 28,870; Robert T. Pous, Reg. No. 29,099; Charles L. Gholz, Reg. No. 26,395; Vincent J. Sunderdick, Reg. No. 29,004; William E. Beaumont, Reg. No. 30,996; Robert F. Gnuse, Reg. No. 27,295; Jean-Paul Lavalleye, Reg. No. 31,451; Stephen G. Baxter, Reg. No. 32,884; Martin M. Zoltick, Reg. No. 35,745; Robert W. Hahl, Reg. No. 33,893; Richard L. Treanor, Reg. No. 36,379; Steven P. Weihrouch, Reg. No. 32,829; John T. Goolkasian, Reg. No. 26,142; Richard L. Chinn, Reg. No. 34,305; Steven E. Lipman, Reg. No. 30,011; Carl E. Schlier, Reg. No. 34,426; James J. Kulbaski, Reg. No. 34,648; Richard A. Neifeld, Reg. No. 35,299; J. Derek Mason, Reg. No. 35,270; Surinder Sachar, Reg. No. 34,423; Christina M. Gadiano, Reg. No. 37,628; Jeffrey B. McIntyre, Reg. No. 36,867; and Paul E. Rauch, Reg. No. 38,591; our (my) attorneys, with full powers of substitution and revocation, to prosecute this application and to transact all business in the Patent Office connected therewith; and we (I) hereby request that all correspondence regarding this application be sent to the firm of OBLON, SPIVAK, McCLELLAND, MAIER & NEUSTADT, P.C., whose Post Office Address is: Fourth Floor, 1755 Jefferson Davis Highway, Arlington, Virginia 22202.

We (I) declare that all statements made herein of our (my) own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

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